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Properties of LaB_6 elucidated by density functional theory

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Although lanthanum hexaboride has been routinely used as a cathode material in commercial devices for over 20 years, a microscopic explanation for its amazing electron-emission properties is still lacking. We present results of *ab initio* calculations, which reproduce the observed low work function, identify an as yet unreported surface state partly responsible for the emission, and yield consistent values for the heat of evaporation of La and B atoms from the surface, as well as for the migration enthalpy of La in the bulk. Our computed surface phonon spectral density compares well with that measured by high-resolution inelastic electron scattering. Bulk phonon dispersion relations, obtained in the frozen phonon approximation, show the rapid flattening of the acoustic branches observed in this class of materials by inelastic neutron scattering.

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Lanthanum hexaboride is the choice cathode material in electron microscopes and especially in electron-beam lithography devices, due to its high electron emissivity, low work function, and longevity. Although the potential of LaB_6 as a thermionic emitter has been recognized over half a century ago by Lafferty[1] in his seminal study of the work function and atom-evaporation rate of this and other hexaboride compounds, it is still not clear why so polar a system should display this property. Lanthanum hexaboride crystallizes in a simple cubic lattice, with B_6-octahedra in body-centered positions and La ions at the corners of the unit cell, as shown in Fig. 1. The structure allows for large, apparently uncorrelated excursions of the lanthanum ions from their equilibrium positions, reflected in the almost dispersionless acoustic branches of the phonon spectrum away from the center of the Brillouin zone (BZ).[2] Two of the three electrons donated by the cation saturate the covalent bonds of the boron network, the third one is responsible for the high metallic conductivity[3,4] (roughly one fifth of that of copper) of the material.

The hexaborides are most easily cleaved along one of the (001) directions by cutting the covalent bonds between B_6 octahedra. A tunneling electron microscopy study[5] and other experiments[6] have confirmed Lafferty's speculation that the exposed [001] face consists of a monolayer of La atoms, and shown that these form a 1×1 structure in perfect registry with the bulk. From a phenomenological analysis of the surface phonon dispersion obtained by high-resolution electron energy loss spectroscopy (HREELS), Nagao and collaborators[7,8] have concluded that the surface La layer suffers a slight outward relaxation. Earlier angular-resolved x-ray photoemission spectra have been interpreted in terms of an unrelaxed surface.[9] From similar experiments in the ultraviolet range (UPS), work functions between 2.1 and 2.4 eV have been inferred for that face at room temperature.[9–11]

In this article we present theoretical results for the lattice relaxation, the work function, and the surface electronic states on the [001] face of LaB_6, as well as for the frequencies of the bulk and surface phonon modes of this system, extracted from *ab initio* calculations on periodically repeated supercells consisting of (001)-oriented, symmetric, lanthanum-terminated slabs of LaB_6 containing (for the surface calculations) up to 13 La planes, separated by a vacuum region with a width of up to 12 lattice constants,[12] using the generalized gradient approximation[13] to density functional theory.

The bulk phonon dispersion relations obtained in the frozen phonon approximation are compared with the measured ones[2] in Fig. 2. We reproduce the almost flat dispersion of the acoustical branches away from the center of the BZ and find slight anomalies that can be traced back to nesting features of the Fermi surface,[14,15] but which were not completely resolved in the experiment. It is worth mentioning that such anomalies were indeed seen in the isostructural compound SmB_6.[16] The lowest set of computed optical branches is in good agreement with the observed ones along the Γ-X direction, but there is a qualitative difference be-

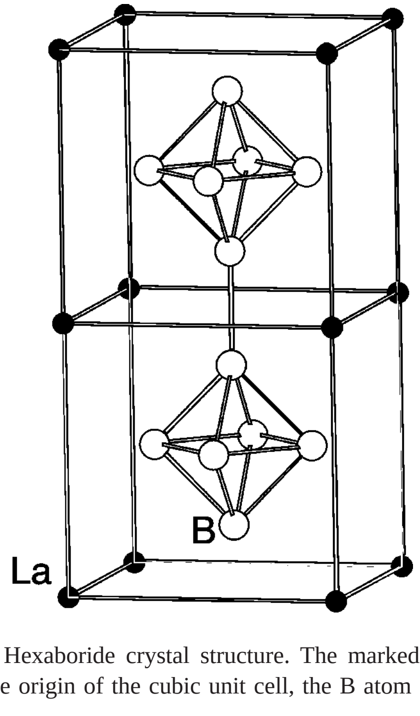

FIG. 1. Hexaboride crystal structure. The marked La atom is placed at the origin of the cubic unit cell, the B atom at $\left(\frac{1}{2},\frac{1}{2},x\right)$.

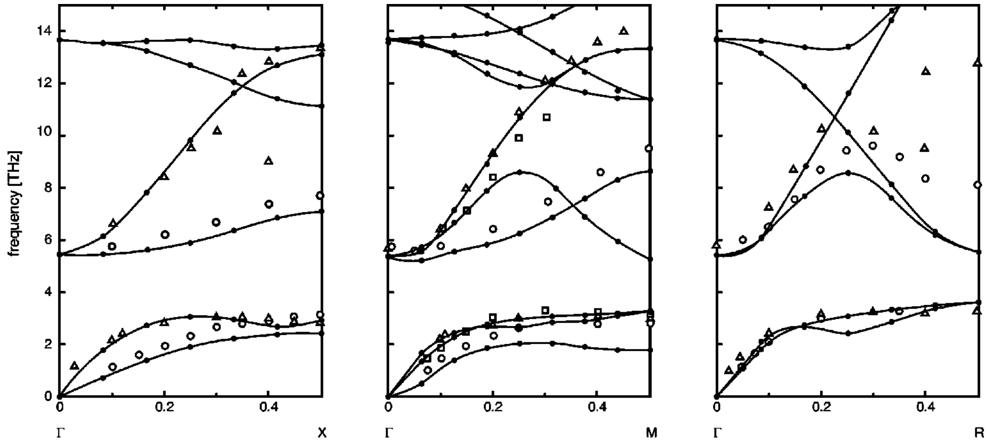

FIG. 2. Phonon dispersion curves for LaB_6. The black dots are the computed values, the open symbols are inelastic neutron scattering results from Ref. 2. The abscissa is in units of the reduced wave-vector coordinate $\zeta = aq_{x(y,z)}/2\pi$.

tween the calculated and measured behavior of one of the TO modes along the Γ-*M* and Γ-*R* directions. As mentioned by the authors of Ref. 2, measurements out to the BZ boundaries were difficult because of the small size of the sample and the lower neutron flux available at higher energies, and it is therefore not unlikely that some excitations were missed in the experiment. This conjecture is supported by the strong similarity between our computed dispersion curves and those observed in SmB_6.[16]

Upon cleavage, new phonon modes appear, localized on the outermost layers of the crystal, and which describe vibrations of the ions around their equilibrium positions *in the presence of the surface.* These new equilibrium positions, we have found, differ substantially from the ones in a rigidly cleaved bulk or from the ones suggested in Refs. 7 and 8. In particular, the interlayer spacing betweeen the surface lanthanum layer [La(1)] and the subsurface boron layer [B(2)] is reduced by 44%! The relaxed positions of the six lattice planes closest to the surface are summarized in Table I. The calculated relaxation pattern is readily understood if account is taken of the polar nature of the compound: in the bulk, the cations are symmetrically attracted by the surrounding, negatively charged boron ions, and their equilibrium position is at the center of the unit cell. The semi-infinite system has no more anions in the vacuum region, which results in a net attraction towards the inside of the crystal for the surface La (1) plane. This, in turn, increases the interaction of this plane with the subsurface boron layer, causing the latter to move outwards, but by a smaller amount, partly because of the rigidity of the boron network, partly because of the attraction by the next plane of La(5) ions, which has ”followed” the boron layer. The elongation of the outermost boron octahedra along the surface normal is accompanied by a 0.4% reduction of their lateral size. The net energy gain resulting from the geometrical relaxation process amounts to 0.4 eV per surface unit cell.

TABLE I. Relaxation of the first six lattice planes at the [001] face of La-terminated lanthanum hexaboride in percent of the bulk lattice constant $a = 4.156$ Å. + (−) stands for outwards (inwards) relaxation.

La(1)	B(2)	B(3)	B(4)	La(5)	B(6)
−6.5	+2.3	+0.5	0.0	+1.2	0.0

The surface phonons for the [001] face of LaB_6 have been measured by HREELS along the Γ-*M* direction of the surface BZ.[7,8] Their dispersion is rather weak, which allows a direct comparison between the corresponding spectral distribution and the computed frequency spectrum at the center of the BZ (Fig. 3). The calculations reproduce the eight observed branches and confirm the assignments made by the authors of Refs. 7 and 8 on the basis of their phenomenological model: the low frequency region involves only the motion of the outermost La atoms, La-B hybridized excitations appear in the frequency range between 180 and 300 cm^{-1}, and the high-energy phonons are associated with the vibrations of the surface and subsurface boron atoms. The computed peak positions are in rather good agreement with the measured ones.

The work function, defined as the difference between the electrostatic potential in the middle of the vacuum region between two symmetric slabs and the Fermi level, converges to a value of 2.45 eV for the unrelaxed surface. Intuitively, one would expect the above-described lattice relaxation to

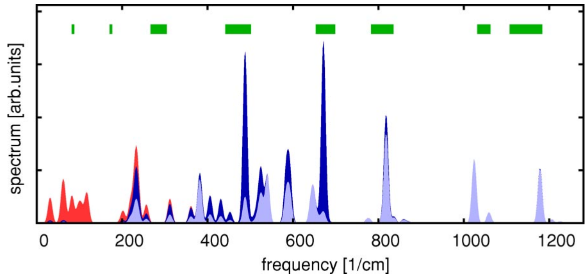

FIG. 3. (Color online) Calculated [001] surface phonon spectral density of LaB_6 at the Γ point of the BZ, for a 5-unit-cell-thick, La-capped slab. In red (gray), projection on surface La, in dark blue (black), projection on surface B, in light blue (light gray), projection on subsurface B. A Gaussian broadening with a half width of 5 cm^{-1} was used. The experimental spectral ranges at the top of the figure are from Ref. 7.

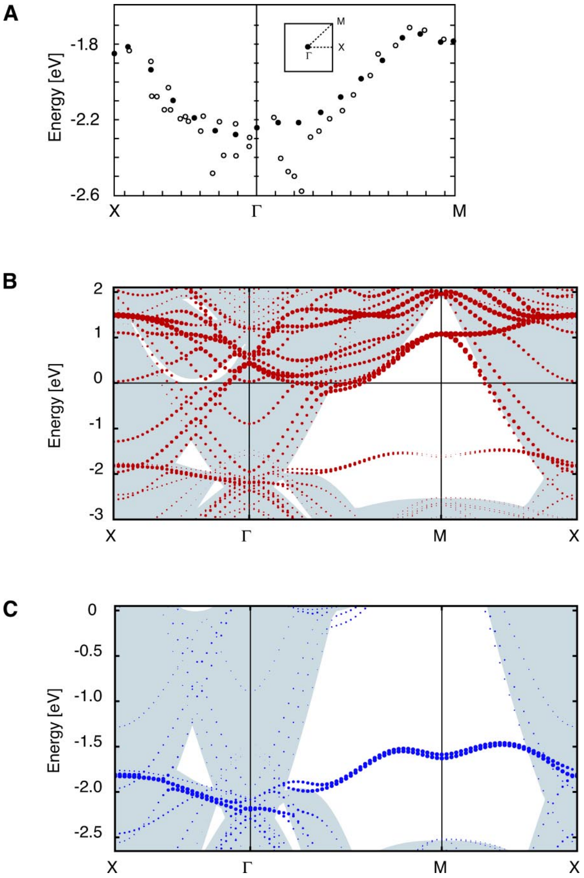

FIG. 4. (Color online) Experimental dispersion of the La(1)-B(2) surface band on the LaB_6 [001] face (from Ref. 17), B [001]-projected bulk band structure of LaB_6 (gray shading) and band structure of a five-layer, La-capped slab, weighted by the Mulliken population of the corresponding states on the La(1) atoms, C same as B, but with the weight given by the Mulliken population on the B(2) atoms. All energies are measured from the Fermi level. The weights are proportional to the size of the dots.

increase the work function. Our calculations show that, on the contrary, the work function is reduced to 2.27 eV upon relaxation, a value in excellent agreement with the one determined by UPS.[11] Whereas in a naive picture, the cation as a whole moves inwards, yielding a net positive contribution to the surface dipole barrier, in reality the direction of the shift in the work function upon relaxation is determined by a subtle redistribution of electronic charge in the outermost region of the slab, leading to the formation of a bonding, hybrid La (1)-B(2) surface band about 2 eV below the Fermi level E_F, as observed by angular-resolved UPS,[17] and illustrated in Fig. 4. There, one also sees that the high electron emissivity of the [001] surface of LaB_6 is partly due to the presence of a band whose spectral weight is strongly localized on the La (1) plane, and which crosses E_F along the Γ-M direction of the surface BZ.

LaB_6 cathodes are typically operated between 1800 and 2000 K. In this temperature range, lanthanum atoms evaporate from the surface at a rate of ~0.006 (1800 K) to ~0.4 (2000 K) monolayer per second,[1,18] congruently with boron;[18] i.e., at the same composition in the gas as in the solid. A measure for the La evaporation rate is given by the partial enthalpy of vaporization ΔH_{La}, which can be obtained from the difference in formation energy between a slab capped on both sides by La, and one from which one of the caps has been removed. In order to avoid the problem of the macroscopic dipole moment arising in the latter situation, we have performed the calculation for that case on a periodically repeated, mirror-symmetric sandwich composed of two slabs, each consisting of seven unit cells of vacuum, four unit cells of LaB_6, followed again by seven unit cells of vacuum. In such a geometry, atoms of the same species face each other across a vacuum region 14 lattice constants thick. Our calculation yields $\Delta H_{\mathrm{La}} \approx 194$ kcal/mole (8.4 eV/atom), which can be compared to the value of 169 kcal/mole quoted by Lafferty[1] and that of 194.3 ± 0.3 kcal/mole reported by Storms and Mueller[18] for a sample containing 1.2% of La vacancies. The computed formation energy of a La vacancy in the bulk is 8.0 eV. This defect is particularly important, as it controls the diffusion of lanthanum from the bulk to the surface. The migration enthalpy of a La ion, obtained as the difference in total energy between a situation where the diffusing ion is at the saddle-point position between two vacancies, with the lattice fully relaxed, and that where the La ion is at its equilibrium lattice site and nearest-neighbor to a vacancy is $\Delta H_{mig} = 5.9$ eV. Assuming that the jump probability of a vacancy per second can be put in the canonical form, as

$$p = \nu^* \exp(-\Delta H_{mig}/k_{\mathrm{B}}T), \tag{1}$$

the effective attempt frequency ν^* at 1800 K would have to be $\sim 2 \times 10^{14}\ \mathrm{s}^{-1}$ in order for each evaporating La atom to be replaced by one diffusing from the bulk. This is substantially higher than the typical rattling frequency of the La ions in their boron cages, $\nu \sim 3 \times 10^{12}\ \mathrm{s}^{-1}$, corresponding to the flat part of the acoustic branches in Fig. 2. Accounting for the entropy of diffusion[19] is not expected to increase ν by much, and our results therefore support the experimental conclusion of Ref. 18 that diffusion is much slower than vaporization in that system at its operating temperature. The partial enthalpy of vaporization for the congruent evaporation of boron with lanthanum, obtained as the difference between half of the formation energy of the above-described sandwich and that of a three-unit-cells-thick slab capped by lanthanum, is $\Delta H_{\mathrm{B}} \approx 147$ kcal/mole, which compares well with the experimentally measured 139.9 ± 0.4 kcal/mole.[18] This relatively low value implies that the average residence time of a boron atom at the surface is much smaller than that of lanthanum atom, which greatly favors the thermoemission process.

In conclusion, we have shown that modern methods of electronic structure theory give a rather complete and consistent picture of the behavior of lanthanum hexaboride. In particular, they have allowed us to identify a surface band as a major source of the high electron yield that makes LaB_6 so useful for practical applications.

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[12] The calculations have been performed with the DMOL^3 code and used the DNP basis set [B. Delley, J. Chem. Phys. **92**, 508 (1990); **113**, 7756 (2000)]. This basis set includes numerical atomic response functions of s, p, d (and f for La) character in addition to the exact numerical solutions for the density functional atom, and is expected to give better than 1 mHartree total accuracy per atom in general. The basis functions have finite tails to help linear scaling methods for all except obtaining the density matrix by diagonalization. Tail lengths have been varied between 9 and 12.5 a.u. for boron and between 9 and 17 a.u. for lanthanum. **k**-space integrations have been performed with a shifted $6\times6\times2$ Monkhorst-Pack [Phys. Rev. B **13**, 5188 (1976)] mesh for the $1\times1\times5$ supercells, which amounts to six symmetry unique **k** points. A thermal broadening of 2 mHartree has been used. The total energy has been modified with the entropy term proposed by M. Weinert and J. W. Davenport [Phys. Rev. B **45**, 13709 (1992)] to make the energy functional variational. The computed ground state lattice constant a, and internal coordinate x are 4.156 Å and 0.201, respectively, which can be compared to the experimental values at 10 K, 4.1527 Å, and 0.1993 given by C. H. Booth *et al.* [Phys. Rev. B **63**, 224302 (2001)].

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[15] Our Fermi surface (FS) topology is in excellent agreement with the one observed in Ref. 14 using the de Haas–van Alphen effect. The FS consists of spheroids, centered at the X points of the simple cubic BZ and prolate along the Γ-X axes, connnected by small necks orthogonal to the Γ-M directions. Our values for the areas of the extremal orbits on these spheroids, with the field along the [001] direction, are within 3% of the measured ones, without any readjustment of the Fermi level. The computed calipers in the XRM plane are 10.0×10^7 cm^{-1} along the MXM direction and 9.36×10^7 cm^{-1} along the RXR direction, which can be compared to the experimental values 10.2×10^7 cm^{-1} and 9.41×10^7 cm^{-1}. The size of the necks is extremely sensitive to the value of the Fermi energy, and an upwards shift of the latter by $\sim$13 meV brings the spheroids into contact. This "latent change in FS topology" results in the anomalies observed in the acoustic branches of the computed phonon spectrum along Γ-M.

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