Electronic, dynamical, and thermal properties of ultra-incompressible superhard rhenium diboride: A combined first-principles and neutron scattering study

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(Received 27 August 2007; published 19 November 2007)

Rhenium diboride is a recently recognized ultra-incompressible superhard material. Here we report the electronic (e), phonon (p), e-p coupling, and thermal properties of ReB2 from first-principles density-functional theory calculations and neutron scattering measurements. Our calculated elastic constants \(c_{11} = 641\) GPa, \(c_{12} = 159\) GPa, \(c_{13} = 128\) GPa, \(c_{33} = 1037\) GPa, and \(c_{44} = 271\) GPa and hardness \(H = 46\) GPa are in good agreement with the reported experimental data. The calculated phonon density of states agrees very well with our neutron vibrational spectroscopy result. Electronic and phonon analysis indicates that the strong covalent B-B and Re-B bonding is the main reason for the super incompressibility and hardness of ReB2. The thermal expansion coefficients, calculated within the quasiharmonic approximation and measured by neutron powder diffraction, are found to be nearly isotropic in \(a\) and \(c\) directions and only slightly larger than that of diamond in terms of magnitude. The excellent agreement found between calculations and experimental measurements indicate that first-principles calculations capture the main interactions in this class of superhard materials, and thus can be used to search, predict, and design new materials with desired properties.

DOI: 10.1103/PhysRevB.76.184113 PACS numbers: 71.20.–b, 62.20.Dc, 63.20.–e, 65.40.–b

I. INTRODUCTION

Hard materials are of great scientific interest due to their numerous technological applications. Unfortunately, almost all superhard materials (diamond, cubic BN, etc.) are expensive because they either occur naturally in limited supplies or have to be made at high pressure synthetically. Therefore, intense research efforts have been carried out to design superhard materials.1 Recently, it was found that rhenium diboride can be synthesized at ambient pressure with potentially low cost, and the resulting ReB2 crystal has superincompressibility along the \(c\) axis, comparable to that of diamond, and high hardness, comparable to that of cubic BN.2 The mechanical properties of ReB2 were also correctly predicted by a recent theoretical work.3 To more fully understand this unusual material, we have used a combined first-principles and neutron scattering study to further investigate the electronic, elastic, phonon, and thermal properties of ReB2.

II. METHODS AND MATERIALS

Our calculations were performed within the plane-wave implementation of the generalized gradient approximation (GGA) to density-functional theory (DFT) in the PWSCF package.4 We used Vanderbilt-type ultrasoft potential with Perdew-Burke-Ernzerhof exchange correlation. A cutoff energy of 680 eV and a \(16\times16\times6\) \textit{k}-point mesh (generated using the Monkhorst-Pack scheme) were found to be enough for total energy to converge within 0.01 meV/atom. Spin-polarized calculations resulted in zero spontaneous spin polarization for the material investigated; thus here we focus on the results from spin-restricted calculations.

Neutron scattering measurements were undertaken at the NIST Center for Neutron Research. The inelastic neutron scattering (INS) measurements were performed with the BT-4 filter-analyzer neutron spectrometer. The neutron powder diffraction was performed with the BT-1 high-resolution powder diffractometer. ReB2 powder sample used in both experiments was synthesized using the method of direct experiments was synthesized using the method of direct heating of the elements (Re and 11B) in vacuum at 1273 K, as reported in Ref. 2. The purpose of using 11B isotope is to avoid the large neutron absorption of normal boron.5

III. RESULTS AND DISCUSSION

ReB2 has a simple hexagonal structure (space group \(P6_3/mmc\)) with experimental \(a = 2.900\) Å and \(c = 7.478\) Å, as shown in Fig. 1(a).6 The two Re atoms occupy the sites \((1/3, 2/3, 1/4)\) and \((2/3, 1/3, 3/4)\) while the four boron atoms occupy the sites \((2/3, 1/3, z)\), \((1/3, 2/3, 1/2 + z)\), \((2/3, 1/3, 1/2 - z)\), \((1/3, 2/3, 1 - z)\) with experimental \(z = 0.048\). We first optimized both the lattice parameters and the atomic positions of the ReB2 structure. The relaxed parameters (without considering the zero point motion), \(a = 2.9007\) Å, \(c = 7.4777\) Å, and \(z = 0.0478\), all agree very well with the experimental values. We note that the crystal structure of ReB2 is quite different from other metal diboride compounds, a majority of which assume MgB2 type structure. In MgB2, boron atoms are on the same plane, with a graphene structure7,8 while they are buckled in ReB2. In addition, Mg is located above the center of B hexagon in MgB2, while in ReB2, Re is located right on top of the B atom. The structural configuration of ReB2 is mainly due to the strong hybridization of Re-\(d\) and B-\(p\) orbitals, which we will discuss in detail below.

To understand the high hardness of ReB2, it is essential to look at its electronic structure. According to the calculated

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1098-0121/2007/76(18)/184113(6) 184113-1 ©2007 The American Physical Society
valence charge distribution, there exist large electron densities between two neighboring B atoms, and between the Re atoms and its neighboring B atoms, indicating strong directional, covalent B-B and Re-B bonding. This is as expected, since a material with large hardness must contain highly directional, short and strong bonds. To get more detailed information about the bonding nature, we performed electron localization function (ELF) analysis and Mulliken bond population analysis. In particular, the ELF plot is very useful in terms of distinguishing different bonding interactions. The value of ELF is in the range of 0 to 1 by definition. High ELF value corresponds to a low Pauli kinetic energy, as can be found in covalent bond. A value of ELF near 0.5 corresponds to delocalized electron density as found in metallic bonding. The ELF plot of the (1 1 2 0) crystal plane of ReB2 is shown in Fig. 1(b). The dominant feature is the rather strong B-B bond (labeled “1”). The two Re-B bonds (labeled “2” and “3”) clearly have different bonding characters. The B-B bond along the c axis (labeled “4”) has a large length, but ELF shows that its contribution to the overall bonding is not negligible. More quantitative bond population analysis (see Table I) confirms that the B-B bonding is very strong and highly covalent, with essentially a double bond nature. Interestingly, the Re and its two neighboring B atoms sitting right above and below it (along the c axis) form anti-bonding, while Re forms strong covalent bonding with all other six B neighbors. In Table I, the real-space force constants between these ions, obtained from the phonon calculation (discussed later), are also shown, which indicate strong B-B and Re-B bonding as well. The B-B and Re-B bonds, all together, form a covalently bonded three-dimensional network.

In Fig. 2(a), we show the electronic band structure of ReB2. The total density of states (DOS) and the partial DOS projected onto atomic orbitals are shown in Fig. 2(b). Clearly, the material is metallic and the electronic structure of ReB2 near the Fermi level is governed by a strong hybridization of Re-\(d\) and B-\(p\) orbitals, which results in the strong covalent bonding of B-B and Re-B. In terms of this bonding characteristic, ReB2 is similar to the previously well studied OsB2, although the latter has an orthorhombic structure. We also note that the density of states at the Fermi level, \(N(E_F)\), is quite high and slightly larger than that of the 40 K superconducting MgB2, raising the question of possible superconductivity in ReB2, which we will address later.

We next discuss the elastic constants of the relaxed ReB2 structure, which was calculated directly. For hexagonal crystal, there are five independent elastic coefficients \(c_{11}, c_{12}, c_{13}, c_{33}\), and \(c_{44}\). Therefore, we applied five symmetry-independent strains (\(\gamma, \gamma, 0, 0, 0, 0\), \(\gamma, -\gamma, 0, 0, 0, 0\), \(0, 0, 0, 0, 0, \gamma\), \(0, 0, 0, 0, 2\gamma, 0\), \(\gamma, \gamma, 0, 0, 0, 0\)) to extract the five unknowns. We used \(\gamma\) of \(\pm 0.005, \pm 0.0075, \pm 0.01, \pm 0.015\). From the least-square fit of the total energy vs strain data, we found that \(c_{11}=641\) GPa, \(c_{12}=159\) GPa, \(c_{13}=128\) GPa, \(c_{33}=1037\) GPa, and \(c_{44}=271\) GPa. The quality of the data fit is excellent. By doubling the strain magnitudes, the fitted elastic constants only change slightly, suggesting that the anharmonicity is negligible in this structure. Note that our calculated elastic constant along the c axis \(c_{33}=1037\) GPa is very large and indeed comparable to that of diamond (\(\approx 1040\) GPa, the largest known elastic

### Table I

<table>
<thead>
<tr>
<th>No.</th>
<th>Bond</th>
<th>Population</th>
<th>Length (Å)</th>
<th>Force constant (eV/Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>B-B</td>
<td>1.96</td>
<td>1.820</td>
<td>4.55</td>
</tr>
<tr>
<td>2</td>
<td>Re-B</td>
<td>0.72</td>
<td>2.257</td>
<td>4.34</td>
</tr>
<tr>
<td>3</td>
<td>Re-B</td>
<td>-0.25</td>
<td>2.227</td>
<td>5.08</td>
</tr>
<tr>
<td>4</td>
<td>B-B</td>
<td>-0.14</td>
<td>3.025</td>
<td>1.36</td>
</tr>
</tbody>
</table>
elastic coefficients with the computational results of Hao which we obtain respectively. For a hexagonal crystal, the Voigt bulk modulus which is also consistent with experimental observation. For a hard materials. The hardness of a covalent or ionic compound can be directly calculated using the method recently proposed by Šimunek and Vackár, based on analyzing bond strengths and their densities. As discussed earlier, in the ReB₂ crystals, each Re atom forms eight bonds with B atoms, six of which have d_{Re-B}=2.257 Å (bonding) while other two have slightly shorter d_{Re-B}=2.227 Å (antibonding). In addition, each B atom forms three covalent bonds with its neighboring B atoms (d_{B-B}=1.820 Å). The Re-Re interaction has a weak metallic nature with a nearest neighbor distance of 2.90 Å, thus their contribution to the hardness is negligible. The reference energies (number of valence electron divided by the radius which makes the atom neutral) for Re and B were calculated to be 4.878 and 3.09, respectively. Using Eq. (6) in Ref. 19, we derived \( H=46.0 \) GPa. Although the anisotropy of the hardness was not considered here, the calculated average value falls right within the range of the experimentally measured hardness (\( \approx 30 \) to 56 GPa).

Next, we discuss the phonon structure of ReB₂, which also reflects the mechanical properties. In addition, the lattice dynamics determine a wide range of other macroscopic behaviors such as thermal and transport properties, and the interaction with radiation (e.g., infrared absorption, Raman scattering, or inelastic neutron scattering). We performed the dynamical calculations on the optimized ReB₂ structure using the supercell method with finite difference. A 2×2 supercell was used, and the full dynamical matrix was obtained from a total of eight symmetry-independent atomic displacements (0.02 Å). The unit cell of ReB₂ contains six atoms, which give rise to a total of 18 phonon branches. The phonon modes at \( \Gamma \) are classified as

\[
\Gamma(q=0) = A_{1g} + 2A_{2u}(IR) + 2B_{1g} + B_{2u} + E_{2u} + 2E_{2g}(R) + 2E_{1u}(IR) + E_{1g}(R),
\]

where \( R \) and IR correspond to Raman and infrared active, respectively. The crystal symmetry implies six Raman- and six IR-active modes. In Table II, we list the calculated energies at \( \Gamma \) and corresponding mode characters.

The computed phonon dispersion curves and phonon density of states are shown in Fig. 4(a). The acoustic branches have steep slopes, indicating large elastic coefficients. Using the low-energy part of the acoustic branches (i.e., “elastic limit”), we can estimate the sound velocity (\( V \)) and thus also elastic constants. For example, for a hexagonal crystal, \( c_{33} = \rho V_l (\text{longitudinal [0001]})^2 \) and \( c_{44} = \rho V_t (\text{transverse [0001]})^2 \), where \( \rho \) is the mass density. We derived \( c_{33}=948 \) GPa and \( c_{44}=278 \) GPa. The slope determination close to \( q=0 \) certainly has some error bar; nevertheless, the above estimated values are still in reasonable agreement with the more precise numbers calculated earlier by directly applying strains.

The optical phonon branches are clearly divided into two groups. The three lowest energy optical modes (\( \approx 30 \) meV) are dominated by Re motion while the high energy optical modes (\( \approx 50 \) meV) are dominated by the lighter B atom displacement. Note that for similar types of atom motion, we found that those along \( c \) axis always have higher energies than the one within the basal \( a-b \) plane. This is due to the covalent Re-B bonding along the \( c \) axis. For boron motion within the plane, those involving B-B bond stretching (i.e., the motion of the bonded B-B pair being out-of-phase) are of higher energy than the in-phase motion, due to the strong B-B covalent bonding. Hence, the phonon structure is totally consistent with our earlier electronic structure analysis.

The calculated phonon structure is further validated by the neutron spectroscopy measurement. The measured INS spectrum is essentially the phonon DOS weighted by the neutron

\[
\frac{\delta N(E)}{dE} = \sum_{\Gamma} \frac{g_{\Gamma}}{N_{\Gamma}} \frac{2\pi}{h} \frac{\rho_{\Gamma}}{\rho} \frac{1}{V} \frac{d\omega_{\Gamma}^2}{dE} f(E_E\omega_{\Gamma}(\omega_{\Gamma}, E_E)),
\]

where \( f \) is the Fermi-Dirac function, \( \rho_{\Gamma} \) is the number of states in the zone \( \Gamma \), \( V \) is the volume, \( \omega_{\Gamma} \) is the energy of the phonon modes, and \( E_E\omega_{\Gamma}(\omega_{\Gamma}, E_E) \) is the energy of the neutron interaction with radiation (e.g., infrared absorption, Raman scattering, or inelastic neutron scattering).
scattering cross sections of the elements. As shown in Fig. 4, the agreement between the experimental data and the calculated spectrum based on the incoherent approximation is excellent.

It is interesting to note that the phonon structure of ReB$_2$ is quite similar to that of MgB$_2$, a high-$T_c$ material. With a MgB$_2$-like phonon spectrum and a slightly higher $N(E_F)$ than that of MgB$_2$ as mentioned earlier, one may wonder if ReB$_2$ can exhibit superconductivity at a "high" temperature. Experimentally, in the Re-B system, Re$_3$B and Re$_7$B$_3$ were found to have a $T_c$ of 4.8 and 3.3 K, respectively. We are not aware of any experimental measurement of $T_c$ in ReB$_2$. We thus calculated the electron-phonon coupling parameters at $\Gamma$ for ReB$_2$ and tried to estimate $T_c$. The results are shown in Table II. The coupling mainly takes place for B phonons along $c$ axis. Compared to MgB$_2$, the electron-phonon coupling in ReB$_2$ is much weaker. Using the McMillian expression and only considering the zone center phonon, $T_c$ of ReB$_2$ is estimated to be less than 1 K. It would be interesting to confirm this estimate experimentally.

Finally, we discuss the thermal expansion of the ReB$_2$ structure, a property important for practical applications. The temperature dependence of the lattice parameters $a$ and $c$ are calculated within the quasiharmonic approximation. The results were obtained by minimizing the Helmholtz free energy:

$$F(a,c,T) = V(a,c) + \sum_j \sum_q \left\{ \frac{1}{2} \hbar \omega_j(q) + kT \ln \left( \frac{1}{e^{\frac{\hbar \omega_j(q)}{kT}}} + 1 \right) \right\},$$

where the first term is the ground-state energy and the second term is obtained by summing the phonon modes over the wavevectors in the Brillouin zone. In the quasiharmonic approximation, the effect of the anharmonicity in the lattice
energy is treated by allowing the phonon frequencies to depend on the lattice parameters. Hence, for a given temperature $T$, we first take $a$ and $c$, minimize the atomic positions, and then calculate the phonon spectrum and the free energy. Repeating this for other values of $a$ and $c$, we find the optimum values of the lattice parameters that minimize the free energy at a given temperature. In this way, one obtains the temperature dependence of $a$ and $c$.

In summary, we have applied density-functional theory and neutron scattering techniques to elucidate the electronic, elastic, phonon, and thermal properties of ReB$_2$. Our calculated elastic constants, bulk modulus, and hardness are in very good agreement with the experimental data. Our electronic and phonon results confirmed that the strong covalent

### IV. CONCLUSIONS

In summary, we have applied density-functional theory and neutron scattering techniques to elucidate the electronic, elastic, phonon, and thermal properties of ReB$_2$. Our calculated elastic constants, bulk modulus, and hardness are in very good agreement with the experimental data. Our electronic and phonon results confirmed that the strong covalent
B-B bonding and Re-B bonding play a critical role in the incompressibility and hardness of ReB$_2$. Our calculations indicate that ReB$_2$ has a very similar phonon spectrum to MgB$_2$ with a comparable $N(E_F)$. However, we found a very small electron-phonon coupling, which suggests a very modest superconducting temperature. The thermal expansion coefficient is found only slightly larger than that of diamond. The combined excellent mechanical and thermal properties suggest great potential for ReB$_2$ to be used as a cutting or coating material. The excellent agreement found between DFT calculations and experimental measurements indicate that first-principles calculations are able to capture the main interactions in this class of superhard materials, and thus can be used to search, predict, and design other materials with properties (hardness, etc.) better than diamond.

ACKNOWLEDGMENT

The authors thank T. J. Udovic for technical help in the INS data collection.

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5 Regular boron contains $\approx$20\% $^{10}$B and $\approx$80\% $^{11}$B. The $^{10}$B isotope has a very large neutron absorption cross section.


