Electron-Phonon Interaction in NbB$_2$: A Comparison with MgB$_2$

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Abstract

We present a comparison of electron-phonon interaction in NbB$_2$ and MgB$_2$, calculated using full-potential, density-functional-based methods in P6/mmm crystal structure. Our results, described in terms of (i) electronic structure, (ii) phonon density of states $F(\omega)$, (iii) Eliashberg function $\alpha^2 F(\omega)$, and (iv) the solutions of the isotropic Eliashberg gap equation, clearly show significant differences in the electron-phonon interaction in NbB$_2$ and MgB$_2$. We find that the average electron-phonon coupling constant $\lambda$ is equal to 0.59 for MgB$_2$ and 0.43 for NbB$_2$, leading to superconducting transition temperature $T_c$ of around 22 K for MgB$_2$ and 3 K for NbB$_2$.

The lack of success in finding superconductivity in other diborides with superconducting transition temperature, $T_c$, close to that of MgB$_2$ [1] underscores the complex nature of interaction responsible for superconductivity in MgB$_2$. In MgB$_2$ the complexity is further compounded by the presence of multifaceted Fermi surface [2,3] and a highly anisotropic electron-phonon coupling, $\lambda(k,k')$, over the Fermi surface [4,5]. The dependence of superconducting properties on such details has ensured that we do not know, as yet, the exact nature of interaction leading to superconductivity in MgB$_2$.

Within Eliashberg-Migdal theory [6,7] of superconductivity, a reliable description of the superconducting state requires an accurate knowledge of $\lambda(k,k')$ and the renormalized electron-electron interaction, $\mu^*$, which are used as input to the fully anisotropic gap equation. The present computational capability allows us to evaluate $\lambda(k,k')$ accurately using density-functional-based methods but, unfortunately, $\mu^*$ cannot be evaluated. However, it is reasonable to assume that $\mu^*$ varies between 0.1 to 0.2 [4,5]. Thus, the electron-phonon coupling $\lambda(k,k')$, which is a normal state function, must contain signatures of superconducting state.
In an attempt to identify some of the unique features of electron-phonon interaction in MgB$_2$ vis-a-vis other diborides we have studied (i) the electronic structure, (ii) the phonon density of states (DOS), (iii) the Eliashberg function, and (iv) the solutions of the isotropic Eliashberg gap equation for NbB$_2$ and MgB$_2$ in $P6/mmm$ crystal structure.

The choice of NbB$_2$ has been motivated by the recent reports [8,9] of superconductivity, with $T_c$ going up to 9.2 K, under pressure in hole-doped Nb$_x$B$_2$. Earlier experiments have shown superconductivity in stoichiometric NbB$_2$ [9,10] as well as Boron-enriched NbB$_{2.5}$ [11] samples. The reported $T_c$ for stoichiometric NbB$_2$ varies from 0.62 K [10] to 5.2 K [9], while for Boron-enriched NbB$_{2.5}$ the $T_c$ is found to be 6.4 K [11]. We also note that, recently, Kaczorowski et al. [12] did not find any superconductivity in NbB$_2$ down to 2 K.

We have calculated the electronic structure of NbB$_2$ and MgB$_2$ in $P6/mmm$ crystal structure with optimized lattice constants $a$ and $c$, as given in Table I. The lattice constants $a$ and $c$ were optimized using the ABINIT program [13] based on pseudopotentials and plane waves. For studying the electron-phonon interaction we used the full-potential linear response program of Savrasov [14,15], and calculated the dynamical matrices and the Hopfield parameter. These were then used to calculate the phonon DOS, $F(\omega)$, the electron-phonon coupling $\lambda(k,k')$, and the Eliashberg function, $\alpha^2F(\omega)$, for NbB$_2$ and MgB$_2$. Subsequently, we have numerically solved the isotropic Eliashberg gap equation [6,7,16] for a range of $\mu^*$ to obtain the corresponding $T_c$.

Based on our calculations, described below, we find significant differences in the phonon DOS and the Eliashberg functions of NbB$_2$ and MgB$_2$. In particular, we find that the average electron-phonon coupling constant is equal to 0.59 for MgB$_2$ and 0.43 for NbB$_2$, leading to superconducting transition temperatures of around 22 K for MgB$_2$ and 3 K for NbB$_2$.

Before describing our results in detail, we provide some of the computational details of our calculation. The structural relaxation was carried out by the molecular dynamics program ABINIT [13] with Broyden-Fletcher-Goldfarb-Shanno minimization technique using Troullier-Martins pseudopotential [18] for MgB$_2$ and Hartwigsen-Goedecker-Hutter pseudopotential [19] for NbB$_2$, 512 Monkhorst-Pack [20] $k$-points and Teter parameterization for exchange-correlation. The kinetic energy cutoff for the plane waves was 110 Ry for MgB$_2$ and 140 Ry for NbB$_2$. The charge self-consistent full-potential LMTO [14] calculations were carried out with the generalized gradient approximation for exchange-correlation of Perdew et al [21] and 484 $k$-points in the irreducible wedge of the Brillouin zone. For MgB$_2$, the basis set used consisted of 3$\kappa$ panels and $s$, $p$, $d$ and $f$ orbitals at the Mg site and $s$, $p$ and $d$ orbitals at the B site. In the case of NbB$_2$, we included 2$\kappa$ panels and $s$, $p$ and $d$ orbitals at the Nb site. In all cases the potential and the wave function were expanded.
The calculated lattice constants \( a \) and \( c \). The experimental lattice constants for \( MgB_2 \) [17] and \( NbB_2 \) are shown in the parentheses.

| alloy  | \( a \) (a.u.) | \( c \) (a.u.) |
|--------|----------------|----------------|
| \( MgB_2 \) | 5.76 (5.834) | 6.59 (6.657) |
| \( NbB_2 \) | 5.81 (5.837) | 6.10 (6.245) |

The site- and \( l \)-resolved electronic densities of states, in \( st/(Ry−atom) \), at the Fermi energy in \( MgB_2 \) and \( NbB_2 \) calculated at the optimized lattice constants using the full-potential LMTO method.

| alloy  | element | \( s \) | \( p \) | \( d \) | \( f \) |
|--------|---------|--------|--------|--------|--------|
| \( MgB_2 \) | \( Mg \) | 0.47   | 0.72   | 0.94   | 0.08   |
|          | \( B \)  | 0.06   | 3.36   | 0.15   | -      |
| \( NbB_2 \) | \( Nb \) | 0.02   | 0.09   | 9.54   | -      |
|          | \( B \)  | 0.07   | 1.34   | 0.19   | -      |

up to \( l_{max} = 6 \). The muffin-tin radii for \( Mg, B, \) and \( Nb \) were taken to be 2.4, 1.66, and 2.3 atomic units, respectively.

The calculation of dynamical matrices and the Hopfield parameters for \( MgB_2 \) were carried out using a \( 6 \times 6 \times 6 \) grid while for \( NbB_2 \) we used a \( 4 \times 4 \times 4 \) grid resulting in 28 and 12 irreducible \( \mathbf{q} \)-points, respectively. For Brillouin zone integrations in \( MgB_2 \) we used a \( 6 \times 6 \times 6 \) grid while for \( NbB_2 \) we used \( 8 \times 8 \times 8 \) grid of \( \mathbf{k} \)-points. The Fermi surface was sampled more accurately with a \( 24 \times 24 \times 24 \) grid of \( \mathbf{k} \)-points using the double grid technique as outlined in Ref. [15].

Here, we like to point out the reasons for carrying out the linear response calculation for \( MgB_2 \) in spite of earlier calculations by Kong et al. [4] and Choi et al. [3,5]. The linear response calculation by Kong et al. is similar to the present approach, while Choi et al. used pseudopotentials and frozen phonon method to evaluate the electron-phonon coupling \( \lambda(\mathbf{k},\mathbf{k'}) \). The present approach differs from the work of Kong et al in the selection of \( \mathbf{q} \)-points and the Brillouin zone integrations. As a result Kong et al. find the average electron-phonon coupling constant \( \lambda = 0.87 \pm 0.05 \), which is much higher than the value of \( \lambda = 0.61 \) as reported by Choi et al. [3,5], as well as the experimental values of 0.58 [22] and 0.62 [23] as deduced from specific heat measurements. Our calculated value of \( \lambda \) is equal to 0.59, in close agreement with the work of Choi et al..

A comparison of site- and \( l \)-resolved electronic density of states of \( NbB_2 \) [24] and \( MgB_2 \) [25] at the Fermi energy is given in Table II. A further
Fig. 1. The phonon density of states $F(\omega)$ of $\text{MgB}_2$ and $\text{NbB}_2$ calculated using the full-potential linear response method as described in the text.

decomposition of the densities of states ($st/Ry$) in terms of cubic harmonics reveals the dominance of $B$ $p$ electrons at the Fermi energy in $\text{MgB}_2$ ($p_{x(y)} = 0.9$, $p_z = 1.55$) than in $\text{NbB}_2$ ($p_{x(y)} = 0.43$, $p_z = 0.48$). In addition, in $\text{NbB}_2$, the $Nb$ $d$-electrons ($d_{x^2-y^2} = 1.83$, $d_{z^2} = 1.66$, $d_{3z^2-r^2} = 2.56$) are present in substantial amount, indicating a more active role for $Nb$ in determining the possible superconducting properties of these materials than played by $Mg$ in $\text{MgB}_2$.

In Fig. 1 we show the phonon DOS $F(\omega)$ of $\text{NbB}_2$ and $\text{MgB}_2$ calculated using the full-potential linear response program as described earlier. For $\text{MgB}_2$ we can clearly identify four significant peaks in the phonon DOS at 33, 53, 79 and 96 $meV$, respectively. The peak at 33 $meV$ is related to the van Hove singularity in the acoustical mode [5], and it involves the motion of $Mg$ atom and $B$ atoms separately. However, the region around the peak at 53 $meV$ results from the motion of both $Mg$ and $B$ atoms. The phonon DOS around 79 and 96 $meV$ peaks are due to the coupled motion of $B-B$ atoms in the $x-y$ plane. In particular, the peak at 79 $meV$ corresponds to the in-plane $B-B$ bond stretching mode, and in Ref. [5] it is located at 77 $meV$. Similarly, for $\text{NbB}_2$, the peak in $F(\omega)$ at 32 $meV$ is dominated by the motion of $Nb$ atom, while the region around 65 – 70 $meV$ results from the coupled motion of $Nb$ and the two $B$ atoms. Not surprisingly, 81 $meV$ peak in the phonon DOS of $\text{NbB}_2$ corresponds to the in-plane $B-B$ motion. In contrast with the phonon DOS in $\text{MgB}_2$, the phonon DOS in $\text{NbB}_2$ around 106 $meV$ results from the displacements of both $Nb$ and the two $B$ atoms.

To see the strengths with which the different modes of the ionic motion couple to the electrons, and thus are capable of influencing the superconducting prop-
properties the most, we show in Fig. 2 the Eliashberg function \( \alpha^2 F(\omega) \) of \( NbB_2 \) and \( MgB_2 \) calculated as described earlier. The most striking feature of Fig. 2 is the overall strength of the electron-phonon coupling in \( MgB_2 \) as compared to \( NbB_2 \). We find that the average electron-phonon coupling constant \( \lambda \) is equal to 0.59 for \( MgB_2 \) and 0.43 for \( NbB_2 \), which clearly shows that \( MgB_2 \) is more likely to show superconductivity with a higher \( T_c \) than \( NbB_2 \).

Further analysis of the Eliashberg function, as shown in Fig. 2, reveals the importance of the in-plane \( B - B \) bond-stretching optical phonon mode in \( MgB_2 \), which gives rise to the dominant peak at 79 meV. The other peaks in the phonon DOS of \( MgB_2 \), such as the peaks at 33 and 53 meV, couple weakly with the electrons at the Fermi energy. Thus the motion of Mg atom plays a relatively insignificant role in determining the superconducting properties of \( MgB_2 \). In contrast, in the case of \( NbB_2 \) the phonon modes with peaks at 32, 81 and 106 meV couple to the electrons with almost equal strength, albeit much smaller than in \( MgB_2 \), as can be seen from Fig. 2. We could have expected this because of the significant presence of the \( Nb \) d electrons at the Fermi energy. In Table III we have listed the Hopfield parameter \( \eta \), the electron-phonon coupling constant \( \lambda \), and the various averages of the phonon frequencies for \( NbB_2 \) and \( MgB_2 \). The values listed in Table III for \( MgB_2 \) are in good agreement with the corresponding results of Choi et al. [5].

To examine the superconducting transition temperature, if any, of \( NbB_2 \) and \( MgB_2 \) we have used the calculated Eliashberg function \( \alpha^2 F(\omega) \) to solve numerically the isotropic gap equation [7,16], and the results are shown in Fig. 3 for a range of values of \( \mu^* \). From Fig. 3 we find that for \( \mu^* = 0.1 \) the \( T_c \) for \( MgB_2 \) is equal to \( \sim 23 \) K, while for \( NbB_2 \) it is equal to \( \sim 4 \) K. Thus, our
Table 3
The calculated Hopfield parameter $\eta$, the average electron-phonon coupling constant $\lambda$, the root mean square $<\omega^2>^{1/2}$ and the logarithmically averaged $\omega_{ln}$ phonon frequencies for $MgB_2$ and $NbB_2$.

| alloy  | $\eta$ (mRy/a.u.$^2$) | $\lambda$ | $<\omega^2>^{1/2}$ (K) | $\omega_{ln}$ (K) |
|--------|------------------------|-----------|------------------------|-------------------|
| $MgB_2$ | 167                    | 0.59      | 835                    | 768               |
| $NbB_2$ | 203                    | 0.43      | 669                    | 494               |

calculation shows that $NbB_2$ is superconducting with a possible $T_c$ of around 3 K. It is worthwhile to point out that to obtain a $T_c$ close to that of 39 K for $MgB_2$, as found experimentally [1], one has to solve the anisotropic gap equation [5]. The need to solve the anisotropic gap equation for $MgB_2$ rather than the isotropic gap equation arises due to the highly anisotropic electron-phonon coupling $\lambda(k,k')$ [3–5] over the Fermi surface. In the case of $NbB_2$ the electron-phonon coupling is neither as strong nor as anisotropic, and thus the results obtained with the isotropic gap equation are reliable.

As indicated earlier, the experiments show superconductivity in hole-doped $Nb_xB_2$ under pressure and Boron-enriched $NbB_2$. Hole-doping and Boron enriching both lead to a relative increase in the Boron population at the Fermi energy and, probably, enhances the peak around 81 meV leading to an increase in $T_c$. Of course a more quantitative investigation is needed to pinpoint the exact nature of changes in $NbB_2$ which lead to superconductivity.

In conclusion, we have studied the electron-phonon interaction in $NbB_2$ and $MgB_2$, using full-potential, density-functional-based methods in $P6/mmm$ crystal structure. We have described our results in terms of (i) electronic structure, (ii) phonon density of states, (iii) Eliashberg function, and (iv) the solutions of the isotropic Eliashberg gap equation, which clearly show significant differences in the electron-phonon interaction in $NbB_2$ and $MgB_2$. We find that the average electron-phonon coupling constant is equal to 0.59 for $MgB_2$ and 0.43 for $NbB_2$, leading to superconducting transition temperature of around 22 K for $MgB_2$ and 3 K for $NbB_2$.

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Fig. 3. The superconducting transition temperature $T_c$ as a function of $\mu^*$ for $MgB_2$ and $NbB_2$ as obtained from the isotropic Eliashberg gap equation.

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