Undamped plasmon modes and enhanced superconductivity in metal diborides

Han Gao¹, Chao Ding¹, Wenhui Geng¹, Xikui Ma¹, Yangyang Li¹ and Mingwen Zhao¹,²,∗

¹ School of Physics, State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, Shandong, People’s Republic of China
² Collaborative Innovation Center of Light Manipulations and Applications, Shandong Normal University, Jinan 250358, People’s Republic of China
∗ Author to whom any correspondence should be addressed.
E-mail: zmw@sdu.edu.cn

Keywords: collective excitations, first-principles, metal diborides, plasmons, \(E_{2g}\) phonon, electronic structure, superconductivity

Abstract

The anisotropic geometric and electronic structures of metal diborides (\(\text{MB}_2\)) lead to many unusual optical and electronic properties. Here, we present a first-principles study on the low-energy collective electronic excitations and the superconducting performance of the \(\text{MB}_2\) (\(\text{M} = \text{Be, Mg, Al, and Ca}\)). We demonstrate the undamped cosine-like plasmon modes and the sine-like acoustic plasmons in these metal diborides. Interestingly, the energy of the acoustic plasmons shows a positive correlation with the \(E_{2g}\) phonon modes which are negatively correlated with the superconducting transition temperature (\(T_c\)) of the \(\text{MB}_2\) materials. Moreover, hole doping can lower the energy of the acoustic plasmons and enhance the \(T_c\) of \(\text{CaB}_2\) up to 48.2 K. Our work offers a theoretical guidance to regulate the plasmonic properties, as well as a new predictive factor for superconductivity.

1. Introduction

The discovery of superconductivity in \(\text{MgB}_2\) with a remarkably high superconducting transition temperature (\(T_c\)) ~39 K [1] has stimulated numerous theoretical and experimental explorations to understand the origin of its superconductivity from different aspects, such as band structure [2–4], lattice vibrations [5, 6] and electron–phonon coupling (EPC) [7–9]. Nowadays there is a general belief that \(\text{MgB}_2\) is a phonon-mediated Bardeen–Cooper–Schrieffer (BCS) superconductor with multiple gaps dominated by the strong EPC between the \(E_{2g}\) phonon mode and the two-dimensional (2D) \(\sigma\) bands [2, 3, 8, 10–12]. The strong coupling between acoustic plasmons and optical phonons was expected to alter the dynamical electronic screening and contribute to the superconductivity in layered materials [13–17].

\(\text{MgB}_2\) has a long-lived collective mode with a distinctive cosine-like dispersion between 2.5–4.5 eV with momentum transfer along the [001] (out-of-plane) direction which originates from the \(\pi–\zeta\) inter-band transitions [18–20]. It also leads to many intriguing optical properties, such as strong anisotropic optical conductivity and dichromatism [21, 22]. Additionally, in the region of 0–0.5 eV, an acoustic-like collective mode with a sine-like dispersion emerges [14, 23], which was expected to affect the low-energy dynamical Coulomb interaction and thus the EPC of the systems [14, 23]. Moreover, the lower \(T_c\) of \(\text{BeB}_2\) and \(\text{AlB}_2\) than \(\text{MgB}_2\) [24–27] suggests that the distinct superconductivity in \(\text{MgB}_2\) stems from a delicate balance between electronic and dynamical properties [4, 27–30]. However, the study of the plasmonic properties of these \(\text{MB}_2\) materials has not been reported. The correlation between the acoustic plasmons and superconductivity which is quite crucial for improving the \(T_c\) remains unclear.

In this contribution, we systematically investigated the low-energy collective excitations and the superconductivity in \(\text{MB}_2\) (\(\text{M} = \text{Be, Mg, Ca, and Al}\)) by means of first-principles calculations. We show that the long-lived cosine-like collective excitation commonly exists in these \(\text{MB}_2\) materials, and it is closely related to the local field effect (LFE). The sine-like acoustic plasmon appears in the loss function spectra of...
the most of MB₂ except AlB₂. However, with hole doping, the sine-like acoustic plasmons can be induced in AlB₂. Moreover, an undamped non-dispersive plasmon branch at ~0.5 eV is induced in the hole-doped CaB₂, which remains visible for q beyond the first Brillouin zone (BZ). The acoustic plasmon energy presents a positive correlation with the E₂g phonon modes which is negatively correlated with the Tₑ of the MB₂ materials. A Tₑ as high as 48.2 K is predicted in the hole-doped CaB₂, which is much higher than that observed in MgB₂.

2. Method and computational details

Our first-principles calculations were performed within the framework of density-functional theory (DFT) implemented in the GPAW codes [31]. The interaction between ions and electrons was described by the projector augmented-wave method [32]. The exchange–correlation (XC) function was treated self-consistently with a generalized gradient approximation in the form of Perdew–Burke–Ernzerhof (PBE) [33]. The cutoff energy for the plane-wave expansion was set to 400 eV. The Brillouin zone was sampled by the Monkhorst–Pack scheme with a k-point grid of 0.04π Å⁻¹ to ensure the convergence [34]. The lattice constants and atomic positions were fully relaxed until the atomic force on the atoms was less than 0.01 eV Å⁻¹ and the total energy change was less than 10⁻⁵ eV. The hole doping effect is simulated by extracting extra electrons to the lattices in a homogeneous background charge of opposite sign.

The collective excitation spectra were obtained by using the linear response approach [35]. The non-interacting density response function in the reciprocal lattice space is written as

\[ \chi_{GG'}^0(q, \omega) = \frac{1}{\Omega} \sum_{\mathbf{k} \in \text{BZ}} \sum_{n, \delta} f_n(k + \mathbf{q} - \mathbf{k} + \mathbf{q}) \left( \langle \psi_{\mathbf{n}k}^{\dagger} e^{-iG_1 \cdot \mathbf{r}} \psi_{\mathbf{n}k+q} \rangle \right) \Omega_{\text{cell}}, \]

where the Kohn–Sham energy eigenvalues \( \varepsilon_{nk} \), the wave function \( \psi_{nk} \) and the Fermi distribution function \( f_n \) for the nth band at wave vector \( \mathbf{k} \) was acquired from the ground-state calculations. In the framework of the time-dependent DFT [38, 39], the full interacting density response function can be determined from the Dyson-like equation, which can be expanded in plane-wave basis as

\[ \chi_{GG'}(q, \omega) = \chi_{GG'}^0(q, \omega) \sum_{G_1, G_2} \chi_{GG'}^0(q, \omega) K_{G_1G_2}(q) \chi_{GG}^0(q, \omega), \]

where \( G \) and \( q \) are the reciprocal lattice vector and wave vector, respectively. \( K_{G_1G_2} \) is the kernel including coulomb and XC interaction [40]

\[ K_{G_1G_2} = \frac{4\pi}{|q + G_1|^2} \delta_{G_1G} + f_{xc}. \]

Within the random phase approximation, the second term about XC part can be neglected [35], and the dielectric function is reducible to

\[ \varepsilon_{GG'}^{-1}(q, \omega) = \delta_{GG'} - \frac{4\pi}{|q + G|^2} \chi_{GG'}(q, \omega). \]

The plasmon energy was extracted from the local maximum/peaks of electron energy loss spectrum (EELS) \( L(q, \omega) \), which was calculated from the inverse of the macroscopic dielectric matrix

\[ \varepsilon_M(q, \omega) = 1/\varepsilon_{GG'}^{-1}(q, \omega) \]

\[ L(q, \omega) = -\text{Im}[1/\varepsilon_M(q, \omega)]. \]

In our calculations, a denser k-point grids of 75 × 75 × 57, 76 × 76 × 60, 78 × 78 × 60 and 51 × 51 × 35 were adapted for q-dependent EELS of MgB₂, AlB₂, BeB₂ and CaB₂, respectively. The empty states up to ~50 eV above the Fermi level were involved in the calculations of the response function. An energy cut-off of 50 eV was set in reciprocal space to account for LFE. The broadening parameter \( \eta \) was taken to be \( \eta = 0.05 \) eV.

The EPC calculations were performed using the quantum espresso software package [41, 42] within the framework of density functional perturbation theory [43] and Eliashberg theory [44, 45]. The Eliashberg spectral function can be expressed as

\[ \alpha^2 F(\omega) = \frac{1}{2\pi N(E_f)} \sum_{q'} \delta(\omega - \omega_{q'}) \frac{\gamma_{q'}}{\hbar \omega_{q'}}, \]
Figure 1. (a) Top and side views of the metal diborides (MB$_2$) crystal. Metal and boron atoms are represented by green and orange spheres, respectively. (b) Comparison between the experimental and theoretical collective modes in MgB$_2$. (c) Calculated loss function of MgB$_2$ for the momentum along the $\Gamma$–A direction ($q_z$). The red dashed line indicates the function of $\omega = 0.46 \times |\sin (q_zc)|$.

Table 1. Lattice constants (in Å), acoustic plasmon energy $\omega_{pl}$ (in eV), $E_{2g}$ phonon frequencies (in cm$^{-1}$) at $\Gamma$ and A points, and $T_c$ (in K) in MB$_2$ materials.

| System | a  | c  | $\omega_{pl}$ | $\omega_{E_{2g}}^{\Gamma}$ | $\omega_{E_{2g}}^{A}$ | $T_c$ |
|--------|----|----|-------------|-----------------|----------------|------|
| MgB$_2$ | 3.07 | 3.52 | 0.45 | 575 | 502 | 36.3 |
| BeB$_2$ | 2.93 | 2.88 | 1.24 | 896 | 814 | 3.1  |
| CaB$_2$ | 3.22 | 4.07 | 0.43 | 326 | 294 | 44.4 |
| AlB$_2$ | 3.01 | 3.28 | —  | 964 | 985 | 4.2  |
| h-AlB$_2$ | 3.01 | 3.28 | 0.82 | 739 | 725 | 12.1 |
| h-CaB$_2$ | 3.22 | 4.07 | 0.25 | 236 | 218 | 48.2 |

where $N(E_f)$ is the electron density of states at the Fermi level, and $\omega_{q\nu}$ and $\gamma_{q\nu}$ are the frequency and linewidth for phonon mode $\nu$ at wave vector $q$. The EPC constant $\lambda$ can be determined through BZ summation or frequency-space integration of the spectral function:

$$\lambda = \sum_{q\nu} \lambda_{q\nu} = 2 \int \frac{\alpha^2 F(\omega)}{\omega} \omega \, d\omega$$

in which $\lambda_{q\nu}$ is the EPC constant for phonon mode $\nu$ at wave vector $q$.

According to the McMillan equation modified by Allen and Dynes [46, 47], the superconducting transition temperature $T_c$ can be evaluated using the expression,

$$T_c = \frac{\omega_{log}}{1.2} \exp \left[ \frac{-1.04(1 + \lambda)}{\left(1 - 0.62\mu^* - \mu^*\right)} \right],$$

where $\mu^*$ is an effective screened Coulomb potential, and $\omega_{log}$ is given by

$$\omega_{log} = \exp \left[ \frac{2}{\lambda} \int \frac{d\omega}{\omega} \alpha^2 F(\omega) \log \omega \right].$$

In our calculations, a fine $k$-point grid of $48 \times 48 \times 48$ was employed in determining the EPC strength. The dynamical matrix and EPC matrix elements were calculated on a $6 \times 6 \times 6$ grid. The values of effective
Figure 2. The orbital-resolved band structure of (a) MgB$_2$, (b) BeB$_2$, (c) CaB$_2$, (d) AlB$_2$, (e) h-CaB$_2$ and (f) h-AlB$_2$. The energy of the Fermi level is set to zero.

screened Coulomb potential $\mu^*$ were estimated to be 0.12 (MgB$_2$), 0.09 (AlB$_2$), 0.11 (h-AlB$_2$), 0.10 (BeB$_2$), 0.12 (CaB$_2$) and 0.14 (h-CaB$_2$) by using a full dielectric matrix approach [48, 49].

3. Results and discussion

The $MB_2$ ($M =$ Be, Mg, Ca, Al) materials considered in this work have a hexagonal lattice structure with the space group $P6/mmm$, consisting of alternating honeycomb boron and hexagonal $M$ layers, as shown in figure 1(a). The highly anisotropic band structures due to the layered structure leads to anisotropic superconductivity [50, 51], electrical transport behavior [52] and hyperbolic light dispersion [53, 54]. The lattice parameters of these materials obtained from first-principles calculations are listed in table 1, which agrees well with the experimental and theoretical values in the previous literatures [1, 28, 55–58].

We start from the electronic band structure and collective electronic excitations in MgB$_2$. From the orbital-resolved band structure of MgB$_2$, shown in figure 2(a), we can see that the electronic states near the Fermi level ($E_F$) are dominated by the boron $p$ orbitals, i.e. the $p_{xy}$ orbitals ($\pi$ bands) and $p_z$ orbitals ($\sigma$ bands). The contribution of Mg orbitals, mainly from the $s$ orbital, starts from 1.6 eV above $E_F$ forming the $\zeta$ electronic bands. The $\sigma$ bands locating above $E_F$ are doubly degenerate along the $\Gamma$–$A$ direction, but cross the $E_F$ along the $K$–$\Gamma$ and $A$–$L$ directions, forming hole-pockets along the $\Gamma$–$A$ direction. In sharp
contrast to the flat $\sigma$ bands along the $\Gamma$–$A$ direction (out-of-plane), the three-dimensional $\pi$ bands are highly dispersive along the $\Gamma$–$M$ and $\Gamma$–$K$ directions (in-plane), exhibiting remarkable anisotropic features.

There have been several theoretical works on the collective electronic excitations in MgB$_2$, but most of them have discrepancy in varying degrees with experimental results. Some of the discrepancy can be ascribed to the different approaches in the single-particle state calculations, which underestimated the energy of plasmons by about 0.3–0.5 eV [59]. Here, we calculated the loss function spectra by using an augmented-wave (PAW) method with a uniform real-space grid representation of the electronic
wavefunctions to solve the single-particle states [31]. The two main plasmon modes in the range of 2–8 eV are presented in figure 1(b), where the plasmon energy was extracted from the peak position of the loss functions. Noteworthy, our results are in excellent agreement with the experimental data [59]. Compared with the theoretical results in the previous report [23], the dispersion relation of the plasmon mode along the [100] direction in our calculation is more accordant with \( \omega(q) = \omega_0 + Aq^2 \) [60, 61]. Notably, an acoustic plasmon mode emerges along the [001] direction with a sine-like dispersion relation of \( \omega = 0.45 \times \sin \left( \frac{\pi q}{\sigma} \right) \), as shown in figure 1(c). The above results verify the reliability of our theoretical strategy in calculating the plasmonic properties of MB\(_2\) materials.

We then calculated the electronic band structures of BeB\(_2\), CaB\(_2\) and AlB\(_2\), as shown in figures 2(b)–(d). It is found that these MB\(_2\) crystals have similar electronic band structures as that of MgB\(_2\), except some fine differences. For BeB\(_2\), the doubly degenerate \( \sigma \) bands are more dispersive and locate below \( E_F \) at the \( \Gamma \) point, forming cone hole pockets, as shown in figure 2(b). The occupations of \( \pi \) bands and the position of the \( \zeta \) bands deviate slightly from those of MgB\(_2\). CaB\(_2\) has cylinder hole pockets arising from the doubly degenerate \( \sigma \) bands, as shown in figure 2(c). Compared with MgB\(_2\), the \( \pi \) and \( \zeta \) bands of CaB\(_2\) shift downward relative to the \( \sigma \) bands, so that the Dirac point of the \( \pi \) bands resides exactly at the \( E_F \) and the \( \zeta \) band has an intersection with the \( \sigma \) bands. Such differences can be attributed to the enlarged interlayer distance brought by the larger radii of Ca ions and thus the weaker interlayer coupling between the metal and boron layers. Additionally, CaB\(_2\) has more bands across the \( E_F \), which indicates stronger inter-band transitions. For AlB\(_2\), \( E_F \) is lifted to close to the Dirac point of the \( \pi \) bands due to more electrons in Al than that in Mg, as shown in figure 2(d), the degenerate \( \sigma \) bands are partially filled and far away from the \( E_F \) and fully occupied in AlB\(_2\). Moreover, the \( \zeta \) band contributed by the \( s \) orbitals of metal atoms crosses the \( E_F \) in AlB\(_2\), which is empty in MgB\(_2\). These differences are responsible for the different plasmonic properties of MB\(_2\) materials.

The loss function \( L(q, \omega) \) and dielectric function spectrum \( \text{Im}[\varepsilon] \) of these MB\(_2\) materials are plotted in figure 3. The results of MgB\(_2\) are also presented in figure 3(a) for comparison, which shows good agreement with those reported in previous works [14, 23]. For BeB\(_2\), the in-plane (\( \Gamma-M \)) loss function has only one clear discernible mode (A\(_1\)), as shown in figure 3(b). The A\(_1\) mode manifests a parabolic-like positive dispersion with the energy of \( \sim 3.3 \) eV at small \( q \) and up to \( \omega \sim 4.6 \) eV at \( q \sim 0.47 \) Å\(^{-1}\), acquiring significant width. Besides, an arc-shaped dispersion peak centered around 4.75 eV at \( q \sim 1.25 \) Å\(^{-1}\) is also detectable. Notably, the out-of-plane (\( \Gamma-A \)) loss function differs significantly from that along the in-plane direction. There coexist a cosine-like C\(_1\) mode and a sine-like C\(_2\) mode, similar to that in MgB\(_2\) [14]. The undamped C\(_1\) mode has high intensity particularly in the 1st BZ, and decays completely in the fourth half sinusoidal period (3rd BZ), which can be ascribed to the inter-band transitions between the nearly-parallel \( \pi \) and \( \zeta \) bands [20, 23]. The acoustic C\(_2\) mode is relatively weak in the 1st BZ but strengthened with increasing \( q \) and reaches the maximum intensity at \( q = \pi/c \). In the second sinusoidal period, the intensity of the C\(_2\) mode is greatly weakened but still detectable. The energy ranges of the C\(_1\) mode (4.4–8.1 eV) and C\(_2\) mode (0–1.24 eV) are both wider than that in MgB\(_2\) [14]. Additionally, there is a new plasmon mode (C\(_3\)), higher than the C\(_1\) mode by about 6.5 eV, merges into the C\(_1\) mode at \( q \sim 0.37 \) Å\(^{-1}\). The emergence of these modes can be understood in terms of the dielectric function spectrum. The two branches \( T_1 \) and \( T_2 \) in the dielectric function spectrum of BeB\(_2\) determine the borders of electron–hole continuum. The \( T_1 \) branch starting from 0 eV arises from the \( \pi \) intra-band transitions, and the C\(_1\) mode locates right along the local minimum of \( \text{Im}[\varepsilon] \) above the \( T_1 \) branch. The C\(_3\) mode also starts from a local minimum of \( \text{Im}[\varepsilon] \) at higher energy but submerges into the Landau region rapidly, because of the considerable values of \( \text{Im}[\varepsilon] \) at larger momentum. The acoustic mode can be correlated to the \( T_2 \) branch of the \( \text{Im}[\varepsilon] \) spectrum, and it originates from the intra-band transitions. The C\(_2\) mode resides in the gap between the intra-band \( T_1 \) and \( T_2 \) peaks and propagates along the upper border of the \( T_2 \) branch. Notably, the undamped feature of the cosine-like dispersion is related to the LFE, which leads to the strong coupling between the collective and single-particle excitation channels. The C\(_1\) plasmon mode propagates along the long cosine-like valley channel is detectable in the loss function spectrum.

From the loss function and dielectric function of CaB\(_2\), as shown in in figure 3(c), we can see the in-plane loss function contains several excitation patterns. The most prominent mode at about 3.5 eV (labeled by A\(_1\)) is nearly dispersionless and vanishes at \( q \sim 0.35 \) Å\(^{-1}\). In the out-of-plane loss function spectra, instead of the well-defined cosine-like plasmon mode, there are numerous broad and miscellaneous excitations. We attribute it to the denser bands in the corresponding energy region of CaB\(_2\) and thus stronger mixed inter-band transitions. In the lower energy region, a parabolic plasmon mode, labeled by C\(_1\), appears at \( \sim 1.0 \) eV and disperses to \( \sim 1.8 \) eV at \( q \sim 0.45 \) Å\(^{-1}\). From the dielectric function spectrum, we can identify this mode to an intra-band plasmon mode, because it locates right above the \( T_1 \) branch that starts from 0 eV. Moreover, the sine-like C\(_2\) acoustic plasmon also exists in CaB\(_2\), with the energy range of 0–0.43 eV. However, in comparison with that in MgB\(_2\) and BeB\(_2\), the amplitude of this mode is significantly...
reduced [14]. This can be interpreted by the small slope of the $T_2$ branch and large values between the $T_1$ and $T_2$ branches, which makes the channel of C2 mode can not be dredged. Therefore, as the acoustic plasmon is stimulated, it will be heavily Landau-damped and weakened.

AlB$_2$ has two parabolic-like dispersion modes in the in-plane loss function, as marked by A$_1$ and A$_2$ in figure 3(e). The broader A$_1$ mode has an energy of $\sim 4.2$ eV at small momentum and disperses upward to exceeding 8 eV at large momentum, then finally merges into the single-particle continua. The A$_2$ mode starts from $\omega \sim 2.3$ eV at small momentum and vanishes around 3.4 eV at $q \sim 0.29$ Å$^{-1}$. Besides, there are several additional weak features due to numerous intra-band and inter-band transitions. In the out-of-plane direction, there only exists a long-lived cosine-like C$_1$ mode in the energy range of 3.1–6.1 eV. The C$_1$ mode is narrower and decays more slowly than that in BeB$_2$, and keeps well-defined until the end of the 3rd BZ. These features can be attributed to the new $T_3$ branch appearing in the dielectric function. The $T_3$ branch starting from $\sim 4.5$ eV is due to the $\pi$–$\zeta$ inter-band transitions. Therefore, a local pseudogap between $T_1$ and $T_3$ is formed, making the collective excitation survive and propagate along the channel [13, 62].

Notably, the acoustic plasmon modes found in MgB$_2$ and BeB$_2$ are absent in the loss function of pristine AlB$_2$. It has been demonstrated that the acoustic mode in MgB$_2$ originates from the coherent charge fluctuations between the boron $\sigma$ and $\pi$ bands [14]. We attribute the vanishment of the acoustic plasmon mode to the lifted $E_F$ in AlB$_2$, which suppresses the coherent charge fluctuations between $\sigma$ and $\pi$ bands since the $\sigma$ bands are fully occupied. When the $E_F$ of AlB$_2$ is shifted downward to across the $\sigma$ bands, that is hole doping, the acoustic plasmon mode may be induced.

We therefore considered hole-doped CaB$_2$ (h-CaB$_2$) and AlB$_2$ (h-AlB$_2$) with one hole per unit cell, corresponding to the doping concentration of $2.74 \times 10^{22}$ cm$^{-3}$ and $3.89 \times 10^{22}$ cm$^{-3}$, respectively. The relevant electronic band structures are plotted in figures 2(e) and (f). The $E_F$ of h-CaB$_2$ shifts downward by about 1.0 eV, as shown in figure 2(e). Interestingly, the $\sigma$ and $\zeta$ bands are separated by about 0.5 eV with hole-doping, which means the inter-band transitions below this energy will be suppressed. For h-AlB$_2$, the electronic band structure shows great similarities with that of MgB$_2$, except the positions of $\pi$ and $\zeta$ bands along the A–L–H–A path, as shown in figure 2(f).

The loss function spectrum and the dielectric function of h-CaB$_2$ and h-AlB$_2$ are plotted in figures 3(d) and (f). For h-CaB$_2$ the energy of the A$_1$ mode in the in-plane loss function is improved to $\sim 4.2$ eV and the
peak becomes wider, as shown in figure 3(d). In the large $q$ region, the $A_1$ mode mingles with other weak excitations and expands to a higher energy region. In addition, hole doping also enhances the intensity of the $A_2$ mode. The sine-like acoustic mode ($C_2$) in the out-of-plane loss function spectra becomes weaker and narrower. More interestingly, a nearly dispersionless plasmon mode ($C_1$) at $\sim 0.5$ eV emerges, which can be attributed to the strong hybridization between the $T_1$ and $T_2$ branches in the vicinity of $q = \pi/c$ in the dielectric function. It is long-lived plasmon mode that can propagate across the 1st BZ. For h-AlB$_2$, the energy of $A_1$ mode in the in-plane loss function is slightly increased to 4.6 eV at small momentum but damps more rapidly than that in pristine AlB$_2$, as shown in figure 3(f). The $A_2$ mode disperses from $\omega \sim 3.0$ eV at small momentum and disappears at the energy of 3.9 eV at $q \sim 0.35$ Å$^{-1}$. The intensity of the cosine-like $C_1$ mode along the out-of-plane direction is enhanced and the decay rate is lowered, especially for the large $q$. This is consistent with the response of the dielectric function to hole doping. The dielectric function inside the pseudogap between $T_1$ and $T_3$ branches is reduced, making the channel more unimpeded, which suppress the Landau damping brought by the coupling between the $C_1$ mode and independent-particle excitations. Notably, the acoustic plasmon mode with a sine-like dispersion ($C_2$ mode) appears in the h-AlB$_2$ in a wide energy range from 0 eV to 0.82 eV, accompanied with the appearance of the $T_2$ branch in the dielectric function spectra.

It has been speculated that the acoustic plasmons in transition metals are strongly correlated to their superconductivity [13, 16, 63, 64]. We therefore calculated the EPC and estimated the $T_c$ of the MB$_2$ materials (see table 1). Our calculations show that the $T_c$ of MgB$_2$ and CaB$_2$ can be as high as 36.3 and 44.4 K respectively, consistent with the previous works [1, 65]. Pristine AlB$_2$ is not superconducting at $T > 5$K [27]. Accompanied with the appearance of the acoustic plasmon, the $T_c$ of hole-doped AlB$_2$ is enhanced to 12.1 K. For BeB$_2$, although there is relatively strong acoustic plasmon mode, no superconductivity is observed above 5 K in experiments [24, 29].

The $E_{2g}$ phonon mode is decisive for the high $T_c$ of superconducting MB$_2$ [3, 7, 66]. Our calculations reveal that the frequency of the $E_{2g}$ mode in the MB$_2$ materials can be modulated by the acoustic plasmon and exhibits a positive correlation with the acoustic plasmon energy $\omega_{pl}$, as shown in figure 4(a). Both of the frequencies of $E_{2g}$ mode and the plasmon energy are extracted from the values at the A point ($q = \pi/c$). The loss functions of the MB$_2$ materials in the energy range of 0–2 eV at A point are presented in figure 4(b), where $\omega_{pl}$ corresponds to the peak position of the loss function. For the h-CaB$_2$, $\omega_{pl}$ is determined from the peak position of the loss function at $q = \pi/c$, since the peak at $q = \pi/c$ comes from both $C_1$ and $C_2$ modes. The relation between $T_c$ and $\omega_{pl}$ is presented in figure 4(a). Clearly, $T_c$ has a negative correlation with $\omega_{pl}$. That is, lower acoustic plasmon energy leads to higher $T_c$ in the MB$_2$ materials. More interestingly, a nearly linear relation between $T_c$ and $E_{2g}$ frequency is obtained in figure 4(c). The calculated phonon DOS, Eliashberg spectra function $\alpha^2F(\omega)$ and the integrated EPC parameter $\lambda(\omega)$ are shown in figure 5, from which we can learn that the frequency region of the $E_{2g}$ mode

![Figure 5](image-url)
has the largest contribution to the total EPC. These phenomena are consistent with the previous findings that lower-frequency $E_{2g}$ mode leads to stronger EPC [27, 67, 68]. Therefore, the $\omega_{pl}$ of acoustic plasmons can serve as a predictive descriptor for the superconductivity in the MB$_2$ materials.

4. Conclusion

In summary, on the basis of first-principles calculations, we predict that the undamped cosine-like plasmon mode in AlB$_2$ and BeB$_2$. Acoustic plasmons, which are closely correlated to the superconductivity of transition metal compounds, emerge in MgB$_2$, BeB$_2$ and CaB$_2$, and exhibit a unique sine-like dispersion. Although the sine-like acoustic plasmons is absent in pristine AlB$_2$, but it can be induced by hole doping. Moreover, hole-doping can lead to the emergence of a non-dispersive plasmon in CaB$_2$ along the out-of-plane direction. Interestingly, the energy of the acoustic plasmons presents a positive correlation with $E_{2g}$ phonon modes, and it is negatively correlated to the $T_c$ of these MB$_2$ materials. Importantly, hole doping can reduce the frequency of the $E_{2g}$ phonon modes and enhance the $T_c$ of the MB$_2$ materials. Surprisingly, the $T_c$ of the h-CaB$_2$ is as high as 48.2 K, which is much higher than that observed in MgB$_2$. Our work shows the strong correlation between the plasmonic property and superconductivity in the MB$_2$ materials, which may provide a promising strategy to tune the phonon-mediated superconductivity.

Acknowledgments

This study is supported by the National Key Research and Development Program of China (2016YFA0301200), the National Natural Science Foundation of China (Nos. 11774201 and 12074218) and the Taishan scholarship of Shandong Province.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

ORCID iDs

Mingwen Zhao https://orcid.org/0000-0002-7583-9682

References

[1] Nagamatsu J, Nakagawa N, Muranaka T, Zenitani Y and Akimitsu J 2001 Superconductivity at 39 K in magnesium diboride Nature 410 63–4
[2] An J M and Pickett W E 2001 Superconductivity of MgB$_2$: covalent bonds driven metallic Phys. Rev. Lett. 86 4366–9
[3] Kortus J, Mazin I I, Belaschenko K D, Antropov V P and Boyer L L 2001 Superconductivity of metallic boron in MgB$_2$ Phys. Rev. Lett. 86 4656–9
[4] Medvedeva N I, Ivanovskii A L, Medvedeva J E and Freeman A J 2001 Electronic structure of superconducting MgB$_2$ and related binary and ternary borides Phys. Rev. B 64 020502
[5] Muranaka T, Yokoo T, Arai M, Margiolaki E, Brigatti K, Prassides K, Petrenko O and Akimitsu J 2002 Vibration spectroscopy of MgB$_2$ by neutron inelastic scattering J. Phys. Soc. Japan 71 338–40
[6] Osborn R, Goremychkin E A, Kolesnikov A I and Hinks D G 2001 Phonon density of states in MgB$_2$, Phys. Rev. Lett. 87 077005
[7] Kong Y, Dolgov O V, Jepsen O and Andersen O K 2001 Electron–phonon interaction in the normal and superconducting states of MgB$_2$. Phys. Rev. B 64 020501
[8] Liu A Y, Mazin I I and Kortus J 2001 Beyond Eliashberg superconductivity in MgB$_2$: anharmonicity, two-phonon scattering, and multiple gaps Phys. Rev. Lett. 87 087005
[9] Mazin I I and Antropov V P 2003 Electronic structure, electron–phonon coupling, and multiband effects in MgB$_2$. Physica C. 385 49–65
[10] Tsuda S, Yokoya T, Takano Y, Kito H, Matsushita A, Yin F, Itoh J, Harima H and Shin S 2003 Definitive experimental evidence for two-band superconductivity in MgB$_2$. Phys. Rev. Lett. 91 127001
[11] Choi H J, Roundy D, Sun H, Cohen M L and Louie S G 2002 First-principles calculation of the superconducting transition in MgB$_2$, within the anisotropic Eliashberg formalism Phys. Rev. B 66 020513
[12] Bud’ko S L, Lapertot G, Petrovic C, Cunningham C E, Anderson N and Canfield P C 2001 Boron isotope effect in superconducting MgB$_2$. Phys. Rev. Lett. 86 1877–80
[13] Echeverry J P, Chulkov E V, Echenique P M and Silkin V M 2019 Low-energy collective electronic excitations in LiCa, SrCa, and BaCa. Phys. Rev. B 100 115137
[14] Silkin V M, Balasis A, Echenique P M and Chulkov E V 2009 Ab initio calculation of low-energy collective charge-density excitations in MgB$_2$. Phys. Rev. B 80 054521
[15] Ganguly B N and Wood R F 1972 Acoustical plasmons, phonon anomalies, and superconductivity in transition-metal systems Phys. Rev. Lett. 28 681–4
[63] Geilikman B T 1966 The electron mechanism of superconductivity Sov. Phys. Usp. 9 142–52
[64] Nandakumaran V M 1987 On the role of acoustic plasmons in high $T_c$ superconductors Pramana - J. Phys. 29 113L–5
[65] Choi H, Louie S and Cohen M 2009 Prediction of superconducting properties of CaB$_2$ using anisotropic Eliashberg theory Phys. Rev. B 80 064503
[66] Pesic J, Popov I, Solajic A, Damjanovic V, Hingerl K, Belic M and Gajic R 2019 Ab initio study of the electronic, vibrational, and mechanical properties of the magnesium diboride monolayer Condens. Matter 4 37
[67] Wang Y C, Lv J, Ma Y M, Cui T and Zou G T 2009 Superconductivity of MgB$_2$ under ultrahigh pressure: a first-principles study Phys. Rev. B 80 092505
[68] Choi H J, Louie S G and Cohen M L 2009 Anisotropic Eliashberg theory for superconductivity in compressed and doped MgB$_2$ Phys. Rev. B 79 094518