Phonon anomalies predict superconducting $T_c$ for AlB$_2$-type structures

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We show that the well-known Kohn anomaly predicts $T_c$ for ordered AlB$_2$-type structures. We use $ab$ initio density functional theory to calculate phonon dispersions for Mg$_{1-x}$Al$_x$B$_2$ compositions and identify a phonon anomaly with magnitude that predicts experimental values of $T_c$ for all $x$. Key features of these anomalies correlate with the electronic structure of Mg$_{1-x}$Al$_x$B$_2$. This approach predicts $T_c$ for other known AlB$_2$-type structures as well as new compositions. We predict that Mg$_{0.5}$Ba$_{0.5}$B$_2$ will show $T_c = 63.6 \pm 6.6$ K. Other forms of the Mg$_{1-x}$Ba$_x$B$_2$ series will also be superconductors when successfully synthesised. Our calculations predict that the end-member composition, BaB$_2$, is likely to show a $T_c$ significantly higher than currently achieved by other diborides although an applied pressure $\sim$16 GPa may be required to stabilise the structure.

Introduction

Magnesium diboride, with alternating layers of Mg and B atoms of hexagonal symmetry, is a superconductor below the transition temperature, $^1 T_c \sim 39$ K. Within the MgB$_2$ structure, shown in Fig. 1a and c, the boron layer is critical to the superconducting properties of MgB$_2$. Theory $^2-^4$ and experiment $^5,^6$ demonstrate close links, or coupling, between phonons and electrons. $^7$ Phonons are collective excitations of atoms or molecules in a solid that oscillate at a single frequency and, by their nature, are temperature dependent. Boron vibration frequencies in MgB$_2$ vary with direction in real space. A dominant collective excitation of these atoms – a phonon mode – is designated the E$_{2g}$ mode and is readily detected by Raman spectroscopy. $^8,^9$ The wave vectors and the quantized energies of all atom vibrations are depicted in a phonon dispersion (PD) plot as shown in Fig. 1d. This plot identifies primary reciprocal space directions along the abscissa and, along the ordinate axis, the phonon frequency (or energy). The two in-plane orthogonal E$_{2g}$ modes near the reciprocal space point $G$ are also shown schematically in Fig. 1. These phonon modes are a key to understanding the superconducting properties of MgB$_2$ and metal-substituted forms $^{10-12}$ and, as we will show, provide a simple unambiguous method to calculate $T_c$.

The density functional theory (DFT), which describes the electronic structure of solids in terms of an electron density distribution rather than a many-electron wave function $^{13,14}$ underpins our current understanding of many compounds and, in principle, allows prediction of bulk physical properties. $^{14}$ Analysis and prediction is facilitated by major improvements in computational capacity and use of approximations to address the physics of electronic structure in order to describe electron density for specific crystal structures. $^{14,15}$ For superconductors, many computational methods have been used $^{3,5,16,17}$ to estimate physical properties such as $T_c$. However, predictions of $T_c$ based on DFT band structure calculations alone typically involve estimates of adjustable parameters to ensure theory conforms with experiment. $^{5,7}$ Floris et al. $^{18}$ have shown that superconducting DFT (SCDFT) $^{13}$ can be employed, post facto, to estimate from the electronic band structure a calculated $T_c$ that closely matches experimental data for MgB$_2$. However, this notionally $ab$ initio method employs modifications to standard DFT models $^{13,16,18}$ including new approximations and additional parameterization to close the gap between theory and experiment.

We outline in this paper a method to determine phonon-mediated physical properties using $ab$ initio DFT calculations and interpretation of PDs for AlB$_2$-type structures. We describe an approach to predict $T_c$ that adds no new functionals to standard DFT models $^{19}$ does not invoke free or adjustable parameters $^{16,7}$ and accommodates metal atom substitutions. We use the Mg$_{1-x}$Al$_x$B$_2$ system to demonstrate that $ab$ initio DFT calculation $^{19,20}$ predicts $T_c$ across the compositional range $0.0 < x < 1.0$ based on the magnitude of a phonon anomaly defined by PDs associated with the E$_{2g}$ mode around the $G$-point in reciprocal space. This phonon anomaly is described as a Kohn anomaly along $G-M$ based on inelastic X-ray scattering (IXS) experiments $^5$ on MgB$_2$, which show a softening and broadening of the E$_{2g}$ mode close to $G$. 

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Computational methods

DFT calculations were undertaken using the CASTEP\textsuperscript{19,20} module of Materials Studio 7.0 and a more recent version, Materials Studio 8.0. This module provides the functionality to calculate vibrational properties for a wide range of materials. The linear response within the local density approximation (LDA) and generalized gradient approximations (GGA) with a dense \( k \)-grid mesh is used as detailed in our earlier work.\textsuperscript{9,21}

Calculations are undertaken with an ultra-fine cut-off typically > 990 eV. Convergence criteria for most calculations are as follows: energy at \( 5 \times 10^{-6} \) eV per atom; maximum force at 0.01 eV Å\(^{-1}\); maximum stress at 0.02 GPa and maximum atom displacement at \( 5 \times 10^{-4} \) Å. For BaB\(_2\) calculations, the maximum stress value is varied.

Optimal calculation conditions using CASTEP for the AlB\(_2\)-type structure are given in earlier work.\textsuperscript{9} Ordered superlattice structures for non-end-member compositions within the Mg\(_{1-x}\)Al\(_{x}\)B\(_2\) and Mg\(_{1-x}\)Ba\(_x\)B\(_2\) series are based on geometry optimization of unit cell parameters with \( \text{P6/mmm} \) symmetry. These optimized parameters correlate with experimentally determined values for Al substitutions.\textsuperscript{22} Experimentally determined values for Ba substitutions in the MgB\(_2\) structure are not available. For end-member compositions, optimized unit cell parameters are based on literature values for MgB\(_2\) and AlB\(_2\) as shown in earlier work.\textsuperscript{9,21} Schematic models of crystal structures shown in Fig. 1 are built using optimized cell parameters from CASTEP as input to the program VESTA.\textsuperscript{23} Each schematic shows a unit cell in the \( c \)-axis direction only.

Calculations are undertaken with the High Performance Computing facility at QUT using \( \sim 200 \) cores that are multiples of the \( k \)-grid mesh in \( a \) and \( b \) reciprocal space directions. Within these conditions, PD calculations for the more complex structures may require 7–10 days to achieve dispersion bands with positive values and convergence of the calculation. This requirement may force a compromise in the choice of \( k \)-grid mesh density, the accuracy of results and identification of the anomaly in PD plots.

Electronic band structure calculations for all compositions are consistent with earlier work, in particular, those that invoke a dense \( k \)-grid mesh.\textsuperscript{2,4,16} Electronic structure calculations of substituted compositions also requires consideration of the
k-grid mesh density\(^2\) and, for MgB\(_2\), influences resolution of the tubular sections of Fermi surfaces.

For each composition, calculations on a range of k-grid mesh densities are undertaken to determine the lowest k-value to achieve convergence. For extended superlattice models such as Mg\(_{4}\)AlB\(_{10}\) or Mg\(_{5}\)AlB\(_{12}\), computations for grid sizes between 0.02, 0.025, 0.027 and 0.03, respectively, are evaluated. The lowest k-value to achieve convergence is listed in Table 1 and, for all compositions, k ≤ 0.03 Å\(^{-1}\) although the computational cost increases by a cube power as grid size is reduced.

The values for the k-grid mesh density used in this work are comparable to, or higher than, that used for many PD calculations due to earlier studies\(^4,8,9,24\) that identified key changes in PD characteristics with this parameter. These changes include shifts in E\(_{2g}\) frequency values at specific reciprocal lattice points\(^8,9,24\) and the appearance of vibration mode branches in PD plots.\(^9\)

Computational DFT methods are limited by fundamental assumptions on delocalisation and static correlation embedded in fundamental approximations\(^{25}\) as well as the degree of complexity of material composition and structure,\(^17\) particularly structures containing transition metals.\(^15\) In this work, practical limits include the extent of superlattice models, extension of DFT calculations to include transition metal diborides with substituted compositions and, as noted above, the trade-off between k-grid mesh density, PD detail and convergence. Indications of computational limit for a particular composition in the Mg\(_{1+k}\)AlB\(_2\) series are shown by (a) failure to converge, (b) inconsistent or irregular format of the anomaly in PD plots (e.g. multiple lows and highs of an E\(_{2g}\) mode within one branch) and (c) negative phonon frequency values.

**Stoichiometry and superlattices**

We use superlattices as a computational strategy to model compositions for which x is not an integer. CASTEP\(^{19}\) allows fractional occupancy of specific atoms in a structure for electronic band structure calculations. This structural description is an alternative method to represent intermediate compositions in the Mg\(_{1+k}\)AlB\(_2\) series, but is not possible for PD calculations using CASTEP. Random fractional occupancy of atoms in a solid solution is an alternative approach for CASTEP calculations of band structure. However, this approach induces significant changes in electronic band structures that do not match experimental data. As noted by Kortus,\(^2\) the approach is suited to low levels of metal doping (e.g. x < 0.1) but is expected to fail at higher doping concentrations.

Use of fractional occupancies may invoke inconsistent or uninterpretable shifts in the calculated electronic band structure, particularly in the proximity of the Fermi level. Hence, our PD calculations on ordered compositions do not utilise fractional site occupancies but invoke a superlattice along the c-axis. For superlattice unit cell calculations, appropriate multiples of the end member parameters are used and weighted combinations of these parameters are used as input for mixed compositions containing both Al and Mg or Ba and Mg. A schematic of the ordered composition for x = 0.33, in which an Al layer is sandwiched between two Mg layers, resulting in a 3x superlattice along the c axis, is shown in Fig. 1b. For x = 0.125, the cell size for a DFT calculation can increase to a ~ 3.07 Å and c ~ 28.0 Å. This size cell is the maximum we are able to optimise to then calculate a PD with convergence within a reasonable computational time when limited to <200 cores.

For each superlattice, the degrees of freedom per atom within the sub-lattice unit cell is nine although the number of phonon branches in calculated PDs will depend on the multiples of the super-lattice used to form the P6/mmm unit cell for a specific composition. For structures used in these calculations, Z = 2, 3, 4 or 5 for the superlattice constructs while for the basic P6/mmm structure, such as MgB\(_2\), Z = 1.\(^{26}\) The Fermi energy corresponds to the average electron density of a structure.
and measures the highest energy (in the ground state) of valence electrons in the conduction band as free or nearly free electrons. Therefore, to compare phonon anomalies of end member and intermediate compositions, each superlattice is normalized to a single unit cell.

**Error estimates**

We have described intrinsic sources of error for PD calculations in earlier work.\(^{21}\) Estimates of error in the calculation of \(T_d\) are obtained by measurement of \(\delta\) for both branches of the \(E_{2g}\) mode in the \(G-M\) and \(G-K\) reciprocal directions for each calculation (i.e. for LDA and GGA). Our analysis and estimate of \(\delta\) is dependent on measurement of calculated vibrational frequencies that show a mean relative error\(^ {27}\) of about \(\pm 5\%\) for crystal structures of similar size and complexity to \(\text{MgB}_2\). These values of \(\delta\) are converted to \(T_d\) using eqn \(1\) below. The error estimate is one standard deviation for the values of \(T_d\) determined from all the measured values of \(\delta\). For some compositions, the value of \(T_d\) is an average of up to eight separate estimates of \(\delta\) obtained by measurement of the frequency difference on two branches of \(E_{2g}\) either side of \(G\) for both LDA and GGA models. The individual values for frequency measurements are not shown in Table 1.

![Partial PD plots](image)

**Fig. 2**  Partial PD plots based on DFT models with \(k = 0.02\ \text{Å}^{-1}\) along the \(G-M\) and \(G-K\) directions of reciprocal space: (a) for \(\text{MgB}_2\) and (b) for \(\text{Mg}_2\text{AlB}_6\) using the LDA functional; for the predicted compositions (c) \(\text{MgBaB}_4\) using the GGA functional and (d) for \(\text{MgBa}_2\text{B}_6\) using the LDA functional. The phonon anomalies for the \(E_{2g}\) mode around the \(G\)-point are highlighted in red and the magnitude of the anomaly, \(\delta\), is shown. The dotted red lines show regions with non-degenerate \(E_{2g}\) modes. The green dotted line \(b-b'\) corresponds to reciprocal lattice dimensions equivalent to the average diameter of the Fermi surface for the specific composition. The distance between \(a-a'\) and \(b-b'\) along the \(G-M\) direction is an indicator of coherence length in the \(a-b\) plane of an AlB\(_2\)-type structure.
Results

Phonon anomaly for Mg$_{1-x}$Al$_x$B$_2$

An example of the phonon anomaly for MgB$_2$ calculated using the LDA model with $P6/mmm$ symmetry is given in Fig. 1d and, in closer detail, in Fig. 2a. Fig. 2a shows a portion of the total PD across the $G$–$M$ (right-hand side of the diagram) and $G$–$K$ (left-hand side of the diagram) reciprocal lattice directions. The phonon bands or branches that contain the degenerate $E_{2g}$ modes at the $G$ point and define the double parabolic phonon anomaly are shown in red. The upper limit of the anomaly is defined in this case by the $B_{2g}$ mode at higher energy. For substituted compositions, the $E_{2u}$ or the $B_{2g}$ mode defines the upper extent of the phonon anomaly for $E_{2g}$ bands in the $G$–$M$ and $G$–$K$ directions, as shown in Fig. 2b. For MgB$_2$, we show that these upper modes are important for energy conservation through conversion of phonon energies by coherent relaxation.$^9,21$

In the vicinity of the $G$-point, the $E_{2g}$ PD bands are degenerate and extend along the basal plane directions (i.e., $G$–$K$ and $G$–$M$) with a characteristic inflection along these directions that is limited, or defined, by the $B_{2g}$ mode. Note that outside the anomaly, along the $G$–$K$ and $G$–$M$ directions, the $E_{2g}$ mode changes symmetry to $E_{2u}$ for MgB$_2$. The magnitude of the anomaly, $\delta$, is measured in frequency units (cm$^{-1}$), as shown in Fig. 2. This anomaly is evident in other publications$^9,21,28$ when there is sufficient resolution of the $k$-grid and is referred to as a Kohn anomaly in earlier work.$^5,29$

For high-Al compositions such as Mg$_x$Al$_{6-x}$B$_6$, the frequency difference between $E_{2g}$ and $E_{2u}$ bands at the $G$-point is minimal or zero, and no anomaly occurs. In addition, for these high-Al compositions, the $E_{2g}$ and $E_{2u}$ bands do not show the inflection along the $G$–$M$ and $G$–$K$ directions as we show for MgB$_2$. For AlB$_2$, the $E_{2g}$ mode is the highest frequency optical phonon and does not show a phonon anomaly. $^21$ Similar PD plots for end-member compositions such as MgB$_2$ and AlB$_2$ are described in earlier work$^5,21$ and have been calculated for the compositions shown in Fig. 3 below (open symbols).

Compositional trends

A summary of the modelled parameters for end-member and intermediate compositions of the Mg$_{1-x}$Al$_x$B$_2$ suite is shown in Table 1. The $E_{2g}$ mode for non-end-member compositions in the Mg$_{1-x}$Al$_x$B$_2$ series increases in energy with increase in Al content, as noted previously$^4$ and, in each case, a higher phonon energy (e.g. $B_{2g}$ or $E_{2u}$) occurs until $x = 1$ where $E_{2g}$ is the highest frequency mode.$^9$ These trends are evident with either the LDA or GGA model in the DFT calculation and are consistent with data calculated at sufficient $k$-grid mesh density.$^9$ The calculated values for $E_{2g}$ modes at $G$ shown in Table 1 correspond with experimental values determined by spectroscopic techniques.$^9,30$ Calculated partial densities of phonon states (data not shown) show that Mg and Al contribute almost exclusively to modes below 350 cm$^{-1}$. As noted in earlier work,$^4$ B atoms contribute to modes above 350 cm$^{-1}$ with minor contributions in a small overlap region at 100–350 cm$^{-1}$.

The $E_{2g}$ band is doubly degenerate around the $G$-point along the basal plane directions for non-end-member compositions in the Mg$_{1-x}$Al$_x$B$_2$ series. Fig. 2b shows a portion of the PD around the $G$-point for $x = 0.33$ calculated using the LDA with a $k$-grid mesh value of 0.02 Å$^{-1}$. The two $E_{2g}$ modes, which are degenerate at $G$, are consistent with ordered alternation of boron layers with a metal layer (e.g. either Mg or Al) in the AlB$_2$-type structure. In Fig. 2b, the $E_{2g}$ modes at ~570 cm$^{-1}$ and at ~851 cm$^{-1}$ are highlighted in red, and the higher energy $E_{2u}$ mode is indicated in orange. For this composition, measurement of the anomaly $\delta$ for the lower energy $E_{2g}$ mode shows that it is significantly less (see Table 1) than the anomaly in Fig. 2a. This lower value of $\delta$ is consistent with a dampening of the dominant mode that influences superconductivity in Mg$_{1-x}$Al$_x$B$_2$.

Phonon thermal energy and $T_c$

We have calculated a thermal energy, $T_\delta$, for each composition in Table 1 based on the equation:

$$\delta = (nN/Z)(k_BT_\delta/2)$$

where $\delta$ is the phonon anomaly (in cm$^{-1}$), $n$ is the degrees of freedom per atom, $N$ is the number of atoms per unit cell, $Z$ is the number of formula units per unit cell, $k_B$ is Boltzmann’s constant, and $k_BT_\delta/2$ is the well-known relationship between thermal energy and degrees of freedom.$^9$ Values for the phonon anomaly, $\delta$, when substituted in this equation determine the calculated temperature, $T_\delta$, (in Kelvin) for each composition listed in Table 1.

Fig. 3 shows the calculated temperature (open symbols), $T_\delta$, associated with the phonon anomaly compared with the experimentally determined $T_c$ (solid symbols) for Al content in Mg$_{1-x}$Al$_x$B$_2$. Experimental data for Fig. 3 have been collated from studies that used structure refinements$^{22}$ and/or microstructural and compositional analyses$^{26,31}$ to define stoichiometry and to account for the presence of second phases (e.g. MgB$_4$).$^{26,32}$ These experimental $T_c$ values are for compositions determined on the as-synthesized product(s) made by an internally.
consistent method. The trend towards a lower $T_c$ with increased $x$ value at intermediate compositions for $0.125 < x < 0.5$ is consistent with experimental data\textsuperscript{22,26,31} on well-characterized Mg$_{1-x}$Al$_x$B$_2$. For reference, experimental $T_c$ values for $x = 0.5$ range from ~4 K\textsuperscript{40} to ~13.5 K.\textsuperscript{10,26,34}

We have used this method to estimate $T_c$ on other AlB$_2$-type structures. In these cases, the experimentally determined values for $T_c$ are much lower (~10 K) and thus, features ascribed to a phonon anomaly will be more difficult to detect. The base case for low $T_c$ compounds is provided for the high-Al compositions listed in Table 1 (e.g. Mg$_{0.5}$Al$_{0.5}$B$_2$). However, compositions that do not contain boron atoms may also form in the AlB$_2$-type structure and, in some cases, show superconducting properties.\textsuperscript{35-37} We use the approach outlined above to estimate the $T_c$ of the disilicide compounds BaSi$_2$ and Ca(Al$_{0.5}$Si$_{0.5}$)$_2$. For these disilicides, our estimate for BaSi$_2$ of approximately 0.7 eV to 1.0 eV across the compositional range.

### Phonon anomaly for Mg$_{1-x}$Ba$_x$B$_2$

We show in Fig. 2c and d partial PD plots for MgBaB$_4$ and Mg$_2$Ba$_2$B$_6$. For these DFT calculations, both compositions are constructed as AlB$_2$-type structures with $P6_3/mmm$ symmetry. The extent of the phonon anomaly, $\delta$, is shown for MgBaB$_4$ in Fig. 2c and is similar in form to MgB$_2$ shown in Fig. 2a. Determinations of $\delta$, as shown in Table 2 show that the magnitude of the anomaly for MgBaB$_4$ is significantly higher than for MgB$_2$. Table 2 summarises the calculated parameters for compositions of the Mg$_{1-x}$Ba$_x$B$_2$ series similar to that shown in Table 1. We have calculated fewer compositions for this series compared with the Mg$_{1-x}$Al$_x$B$_2$ series because similar conclusions are evident from these calculations.

Comparison of Tables 1 and 2 shows that the Fermi energies for Mg$_{1-x}$Ba$_x$B$_2$ are lower than the Mg$_{1-x}$Al$_x$B$_2$ series by approximately 0.7 eV to 1.0 eV across the compositional range. In addition, the optical phonons for Mg$_{1-x}$Ba$_x$B$_2$ compositions are typically at lower frequencies than Mg$_{1-x}$Al$_x$B$_2$ with the critical $E_{2g}$ modes at lower frequencies at the $G$ point for equivalent values of $x$.

### Discussion

The Mg-Al diboride system is characterized by a sharp superconducting transition at $x = 0$ that decreases in value and gradually broadens with higher Al content.\textsuperscript{12} Superconductivity in Mg$_{1-x}$Al$_x$B$_2$ is moderated, but not extinguished, by other influences such as order–disorder.\textsuperscript{38} Superlattice(s)$^{10-12}$ and the presence of other phases\textsuperscript{12,33} for $0.0 < x < 0.5$. Band structure calculations,\textsuperscript{2,39,40} experimental data\textsuperscript{41} and phonon calculations\textsuperscript{8} have established that the vibrational properties of the $E_{2g}$ mode for MgB$_2$ influence electron–phonon interactions and superconductivity.\textsuperscript{4,47}

### Ordering and superlattice models

Superlattices are observed in Mg$_{1-x}$Al$_x$B$_2$ systems\textsuperscript{10,11,26,34} with prominent diffraction spots at the reciprocal lattice dimension $c^2/2$, which demonstrate a 2x c-axis superlattice\textsuperscript{24} for Mg$_{0.5}$Al$_{0.5}$B$_2$. Superlattice structures are also predicted\textsuperscript{42} for vacancy-ordered MgB$_2$ but are not considered in this analysis. Detailed analysis of Al-substituted MgB$_2$ shows that superstructures occur for a range of compositions ($x = 0.17^{14}$, $x = 0.25^{10}$, $x = 0.45$, 0.5 and 0.55\textsuperscript{11}) and microstructures.\textsuperscript{10,11} Microstructural studies\textsuperscript{10} suggest that intimate mixtures of MgB$_2$ and Mg$_{0.5}$Al$_{0.5}$B$_2$ may also occur for $0.1 < x < 0.5$. However, the dominant motif involves alternation of Mg and Al layers for $x = 0.5$.\textsuperscript{12} Long range ordering of Al and Mg is observed in the $a$-$b$ plane\textsuperscript{12} with an extent ~10 nm. Representation of this periodicity in the $a$-$b$ plane is non-trivial for DFT calculations and is not considered here. Brutti and Gigli\textsuperscript{38} used DFT calculations to show that for $x > 0.31$, the formation of an Al-rich phase leads to formation of thermodynamically stable Mg$_{0.5}$Al$_{0.5}$B$_2$ at 50% Al concentration in MgB$_2$.

Raman spectroscopy and inelastic neutron scattering studies\textsuperscript{44} on Mg$_{1-x}$Al$_x$B$_2$ samples show evidence for alternate stacking of Mg and Al layers for $x \sim 0.5$. In our earlier work, we note that additional Raman and IR peaks not predicted by $P6_3/mmm$ symmetry for MgB$_2$ are due to super-lattice modes that approximate a dynamic, phonon-distorted lower-symmetry crystal.\textsuperscript{3} We show that a 2x super-lattice in the c-direction allows a simple correlation of the pair breaking energy and the superconducting gap.\textsuperscript{9}

We have evaluated other c-axis ordered structures in which multiple adjacent Al-layers alternate with Mg-layers for key

### Table 2 Calculated parameters for DFT models of Mg$_{1-x}$Ba$_x$B$_2$

<table>
<thead>
<tr>
<th>Ba</th>
<th>Grid</th>
<th>Optimised unit cell parameters</th>
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<th>$E_{2g}$ at $G$ (cm$^{-1}$)</th>
<th>$\delta$ (cm$^{-1}$)</th>
<th>$\delta_{av}$ (meV)</th>
<th>$T_c$ (K)</th>
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<th>$\sigma$(error) (K)</th>
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$^a$ DFT calculation undertaken at equivalent to 16 GPa hydrostatic pressure. $^b$ Average for DFT models: both LDA and GGA models.
compositions (e.g. Mg–Mg–Al–Al for $x = 0.5$ or Mg–Mg–Mg–Mg–Al–Al for $x = 0.33$). In these cases, while there are differences of $\sim 0.15$ eV in calculated enthalpies favouring the stability of single Al-layer stacking, ordered motifs with adjacent Al-layers also show a phonon anomaly similar to that in Fig. 2a and b. Thus, a superlattice repeat along the c-axis utilising a simple alternation of Mg and Al layers to minimise adjacent Al layers is an optimal configuration. For simplicity of computation, we follow a superlattice formalism confirmed by detailed experimental studies\textsuperscript{11,43} and implied by DFT models\textsuperscript{48}

\section*{Phonon anomalies}

The magnitude of the phonon anomaly varies with composition, as do experimentally determined $T_c$ values. The average value of $\delta$ for MgB\textsubscript{2} shown in Table 1 is comparable to the gap energy,\textsuperscript{5} $2\delta$, of $\sim 15$ meV. The variation in magnitude of the phonon anomaly reflects the predominant role of boron layer vibrations in many AlB\textsubscript{2}-type structures\textsuperscript{44,45} and, in this case, the influence of Al substitution on these vibrations. For the AlB\textsubscript{2}-type structure, the $D_{ih}$ point group symmetry results in two E\textsubscript{2g} modes at the G-point and equivalent displacement modes, E\textsubscript{2u}, at the A point of the hexagonal Brillouin zone.\textsuperscript{8}

The doubly degenerate E\textsubscript{2g}(G) band describes two distinct displacement patterns that are equivalent within the harmonic approximation.\textsuperscript{8} The E\textsubscript{2g} and E\textsubscript{2u} modes have the same movement pattern, albeit with different parity (gerade or ungerade), \textit{via} a difference in relative phase.\textsuperscript{8,46} One of the E\textsubscript{2g} modes reflects in-plane B–B bond stretching modes that are strongly coupled to the sigma bonded Fermi surfaces related to the p\textsubscript{x} and p\textsubscript{y} in-plane orbitals.\textsuperscript{46}

Table 1 summarizes the difference in frequency, or the phonon anomaly, $\delta$, between the low and high points of the E\textsubscript{2g} mode inflection for both $G$–$M$ and $G$–$K$ directions for each calculated composition using both LDA and GGA in the Mg\textsubscript{1-x}Al\textsubscript{x}B\textsubscript{2} series. For both DFT calculation methods, the range of values for the phonon anomaly, $\delta$, of each composition is similar, but not equal, because of different assumptions in the methods to calculate the charge distribution in the LDA and GGA methods,\textsuperscript{4} differences in optimized lattice parameters and the k-grid value required to attain convergence.

For each calculated composition in the Mg–Al series, the value of $T_s$ is slightly higher than the experimentally determined values for $T_c$ as shown in Fig. 3. A difference of 1.0 K to 2.5 K is evident for models with $x < 0.25$ and probably relates to factors such as (a) a higher k-grid value (particularly for $x = 0.125$) that allows convergence of the PD calculation, (b) systematic errors associated with extended superlattice construction and (c) our DFT calculations are for absolute zero, ground state properties without correction for higher temperatures. Nevertheless, this \textit{ab initio} determination of $T_s$ is internally consistent and in close agreement with the experimentally determined $T_c$ trends\textsuperscript{22,26,31} for Al-substituted MgB\textsubscript{2}.

The phonon anomaly can be described in terms of interconnected hyperboloid surfaces in different proportions showing origins at different energies and inverse directions along a fixed axis that intercepts G. We can describe this hyperboloid for the E\textsubscript{2g} mode(s) as follows. For the E\textsubscript{2g} dispersion shown in Fig. 1 and 2, the phonon band is in the $k_y - k_y$ plane for which $k_z = 0$. For one hyperboloid, the equation for $k_y = 0$ becomes

$$\omega^2 = \omega_0^2 + d^2(k_y^2 + k_z^2)$$

which is symmetric in the $k_x$ and $k_y$ directions and can be extended to the $k_x - k_y$ plane. Considering only the $k_x$ direction,

$$\omega^2 = \omega_0^2 + d^2 k_x^2$$

The asymptote of the hyperbola described in eqn (3) is $\omega = ak_x$.

The hyperbola can be approximated to a parabolic dependence as below and as commonly encountered in descriptions of the Jahn–Teller effect.\textsuperscript{47}

$$\omega = \omega_0 \sqrt{1 + (a^2/2\omega_0^2)k_x^2}$$

which equals

$$\omega_0 + (a^2/2\omega_0^2)k_x^2.$$ 

Taking the partial derivative of eqn (3), we obtain

$$2\omega \partial\omega/\partial k_x = 2a^2 k_x.$$ 

Since the group velocity, $v_g = \partial\omega/\partial k_x$ and the phase velocity, $v_p = \omega/k_x$, we obtain by substitution

$$v_g = a^2/v_p.$$ 

In the asymptotic region of the E\textsubscript{2g} band, where the phonon dispersion changes abruptly from the lowest point of the anomaly towards the higher E\textsubscript{2u} phonon band, the curve displays an approximate linear behaviour. This behaviour indicates that the group velocity, $v_g$, is constant. From eqn (6), the phase velocity, $v_p$, is also constant.

In the asymptotic region of the E\textsubscript{2g} band, where the phonon dispersion changes abruptly from the lowest point of the anomaly towards the higher E\textsubscript{2u} phonon band, the curve displays an approximate linear behaviour (in Fig. 2, the distance along the $G$–$M$ direction between the green dotted lines $a-a'$ and $b-b'$).

This behaviour indicates that the group velocity, $v_g$, is constant and, as shown above, the phase velocity, $v_p$, is also constant. Therefore, there is an interval of k-vectors, $\Delta k$, relating to phonon waves for which the wave is non-dispersive. That is, the group of waves moves at constant group velocity and each component of the interval also moves at constant phase velocity. In this instance, the wave packet retains shape and can be viewed as a coherent wave. The slope of the E\textsubscript{2g} band in the linear section of the anomaly appears approximately parallel to the acoustic band of highest energy. This relationship suggests that the group velocity of the corresponding optical waves matches the sound velocity.

\section*{Phonons and Fermi surfaces}

Comparison of electronic bands with PDs shows that the phonon anomalies in the Mg\textsubscript{1-x}Al\textsubscript{x}B\textsubscript{2} system originate from cusps of paraboloid bands across the Fermi level in the electronic band structure at the G-point. These anomalies are effected by a transfer of electronic charge from the vicinity of the cusps to and from adjacent unit cells and the flat bands in the G–A direction.\textsuperscript{39,48}
Our calculations show that cusp size is directly proportional to the PD anomaly. For example, the PD anomaly is deep when the cusp size in the electronic band is large. If the cusp dips below the Fermi level, for example as with AlB$_2$, the phonon anomaly does not occur; this is consistent with experimental data\textsuperscript{49} that show no superconductivity for this composition. In addition, for superlattice constructs, multiple parallel cusps that intersect with the Fermi level occur. These intersections are reflected in a multiplicity of E$_{\text{2g}}$ modes and of tubular sections in Fermi surface models.

Calculations of Fermi energies link electrons on or near the Fermi surface to strongly coupled phonons in MgB$_2$.\textsuperscript{39} For example, Fig. 4 shows the Fermi surface for MgB$_2$ calculated with the GGA model for $k = 0.02$ Å$^{-1}$. For this model, the Fermi energy is 8.1087 eV. In a free electron approximation, the Fermi wave vector, $k_F$, is determined from the equation

$$E_F = \frac{\hbar^2 k_F^2}{2m}$$

where $\hbar$ is Planck’s constant, $m$ is the electron mass, and $E_F$ is the Fermi energy. For MgB$_2$, $k_F = 1.458$ Å$^{-1}$. Using reciprocal cell dimensions from our CASTEP calculations, and limiting this analysis to the $k_y$ direction, the Fermi wave vector is $\sim 62\%$ of the magnitude of the first reciprocal space vector $|a_1|^*$. As shown in Fig. 4, the vector resides just outside the first Brillouin zone (point $a$ in the extended zone). Re-plotting this vector to the reduced zone results in $a$ point at position $a'$ on the Fermi surface, as shown in Fig. 4.

For two electrons to interact through a phonon, conservation of energy and momentum give the equation:

$$h(k_y^1 - \hbar k_y^2) = h(k_{\text{ph}} + G)$$

where $k_y^1$ and $k_y^2$ are electron wave vectors, $k_{\text{ph}}$ is the phonon wave vector, and $G$ is a reciprocal space point. For an interaction in the $k_y$ direction, the magnitude of the electron wave vector will be $+k_y$ or $-k_y$. For a pairing mechanism in which electrons with opposite momenta or wave vectors interact, $2k_F = k_{\text{ph}} + G$ for interaction along $k_y$. Substituting values for MgB$_2$ from CASTEP calculations, the ratio of $2k_F$ (after re-plotting to the reduced zone) to $|a_1|^*$ is 0.239. This ratio is equivalent to the point in reciprocal space along the $G$-$M$ direction where the E$_{\text{2g}}$ vibration mode meets the B$_{\text{2g}}$ mode, as shown in Fig. 2a (green dotted vertical line denoted $b$-$b'$). Thus, a one-to-one correspondence between tubular elements of the Fermi surface and the phonon anomaly occurs for this composition. This reciprocal space point is similar for LDA and GGA models of MgB$_2$ with a value $\sim 0.24$ along $G$-$M$ (equivalent to 0.56 Å$^{-1}$). These values are approximately twice the experimentally estimated radii\textsuperscript{5} for cylindrical sigma surfaces parallel to $G$-$A$ which show average values of 0.17 Å$^{-1}$ and 0.25 Å$^{-1}$ using IXS.

For Al-substituted compositions, this point shifts closer to the $G$-point in a PD plot, as shown in Fig. 2b (green dotted line denoted $b$-$b'$; $\sim 0.13$ along $G$-$M$; equivalent to 0.31 Å$^{-1}$). This shift implies a reduction in size of the sigma sheets coupled to the E$_{\text{2g}}$ phonon and is consistent with de Haas van Alfen effect measurements\textsuperscript{50} of Al-substituted MgB$_2$. Our calculations for other compositions (data not shown) also show a size reduction of the cylindrical sigma sheets in Fermi surface projections with increased Al substitution. Al substitution in MgB$_2$ results in a commensurate change in the number of tubular sections in Fermi surface projections in proportion to the multiplicity of E$_{\text{2g}}$ modes using superlattice models.

**Predicted superconducting compositions**

Extrapolation of the methods described above for Mg$_{1-x}$Al$_x$B$_2$ to other compositions\textsuperscript{12,51} of MgB$_2$ and a consideration of diboride thermodynamics\textsuperscript{52} suggest particular atom substitutions to the type structure may also result in superconducting behaviour. For example, our LDA calculations on BaB$_2$ reveal an electronic band structure similar to MgB$_2$ but with a PD that shows unusual frequency variation and negative frequency values for modes in the $A$-$H$ direction and around $G$. Subsequent calculations constrained to include hydrostatic pressure reduced the number and range of negative frequency values. At an applied hydrostatic pressure of 16 GPa convergence of the LDA and GGA models is achieved with phonon anomalies similar to that shown for MgB$_2$ in Fig. 2. The E$_{\text{2g}}$ modes show a strong anisotropy in the PD plot particularly in the $G$-$K$ direction. Nevertheless, these calculations indicate that a BaB$_2$ structure with an applied stress at 16 GPa is likely to show a phonon anomaly, and by inference, superconductivity.

BaB$_2$ is not a well-known compound and may be structurally unstable due to a larger Ba$^{2+}$ ionic radius compared with Mg$^{2+}$. Cava et al.\textsuperscript{12} notes that a variation of approximately 50% of the...
metal atom size can be accommodated by the diboride structure. However, the existence of BaB$_2$ is not readily confirmed. Early literature$^{25}$ on the synthesis of BaB$_2$ reports cell dimensions that are inconsistent with an AlB$_2$-type structure and suggests that this compound is yet to be synthesised. In addition, the geometry optimised cell dimensions for BaB$_2$ shown in Table 2 are comparable to MgB$_2$ for the $a$ axis. The $c$-axis dimension is $\sim 33\%$ greater than the calculated values for MgB$_2$. These attributes, and the unstable nature of DFT models without a hydrostatic pressure constraint, suggest that BaB$_2$ may not be thermodynamically stable except at high pressure.

Our computational method utilises a linear response for both LDA and GGA models and is effective for structures with low anharmonicity. Outcomes from these linear calculations as well as structural considerations (e.g. Ba$^{2+}$ ionic radius), infer that anharmonicity is an important factor for BaB$_2$ PD calculations. An alternative calculation for BaB$_2$ using the Finite Displacement (FD) method at similar hydrostatic pressure shows a PD anomaly very similar to Fig. 2a. In this case, the extent of anomaly is significant ($\sim 250 \text{ cm}^{-1}$) and, by similar analysis to that for DFPT calculations, suggests a $T_c \sim 79.1 \pm 10.2 \text{ K}.$

The result from DFT calculations on BaB$_2$ under an applied stress indicates that substitution of an appropriate valence atom for Ba may also induce a similar shift in structural parameters or an improvement in the calculated PD. DFT calculations for compositions of Mg$_{1-x}$Ba$_x$B$_2$, where $0 < x < 1,$ display phonon anomalies of varying magnitude as shown in Fig. 2c and d. Table 2 lists phonon anomalies for three compositions ($x = 0.333; x = 0.5$ and $x = 0.666$) and for the end-member BaB$_2$ at a hydrostatic pressure of 16 GPa. In all cases, calculated PDs for Mg$_{1-x}$Ba$_x$B$_2$ show a phonon anomaly with an extent significantly greater than calculated for MgB$_2$. This analysis predicts that Mg$_{1-x}$Ba$_x$B$_2$ will show superconductivity at $T_c > 60 \text{ K}$ over a wide compositional range. We infer from the smaller average $c$-axis cell dimensions shown in Table 2 that Mg$_{0.66}$Ba$_{0.33}$B$_2$ is more likely to be a stable phase in this compositional series. This $T_c$ prediction for Mg$_{1-x}$Ba$_x$B$_2$ is $\sim 20 \text{ K}$ higher than that for MgB$_2$, currently the stand-out material in the diboride suite.$^{54}$

Coherence lengths

Using the width $\Delta k$ in reciprocal space, we can derive a width $\Delta x$ in real space that may be associated with the coherence length of the superconductor. Using the calculated PD for MgB$_2$ shown in Fig. 2a, we estimate the coherence length in the $a$-$b$ plane as the distance along the $G$-$M$ direction (i.e. the reciprocal $a$ axis) between the approximately linear sections of the phonon anomaly manifest in the $E_{2g}$ modes. This distance, measured in reciprocal lattice dimensions, can be converted to real space dimensions for the symmetry conditions of the unit cell. For MgB$_2$, our estimate of the coherence length is $\sim 50 \AA \pm 5 \AA$. This value compares favourably with experimentally determined values$^{54}$ between 61 Å and 65 Å for coherence length in the $a$-$b$ plane for single crystals; noting that experimental determination of coherence length is dependent on the applied magnetic field$^{55}$ and temperature.$^{56}$ Similar estimates of coherence length for substituted MgB$_2$ can be inferred from these PD calculations. For Al-substituted MgB$_2$, these estimates of coherence length range from $\sim 70 \AA$ to $\sim 80 \AA$ with increasing Al content. For Mg$_{1-x}$Ba$_x$B$_2$, estimates of coherence length range from $\sim 30 \AA$ to $\sim 50 \AA$ in the $a$-$b$ plane.

Conclusions

We have utilised $ab$ initio DFT calculations to show that PD plots of AlB$_2$-type structures including Mg$_{1-x}$M$_x$B$_2$ (where $M = \text{Al or Ba}$) and MSi$_2$ (where $M = \text{Ca, Al or Ba}$) are key indicators of physical properties. For known compositions, the phonon anomaly predicts physical properties such as the presence (or absence) of superconductivity in this structure type. The extent, or size (in frequency units), of the anomaly provides an estimate of $T_c$ by the well-known relationship between thermal energy and degrees of freedom for a particular structure. Agreement between theory and experiment is strong even though DFT models ground state properties at absolute zero temperature. In addition, this approach does not use modified functionals or post facto corrections and is unable, at this time, to account for time dependent phenomena. The phonon anomaly for the AlB$_2$-type structure is also known as a Kohn anomaly. If present, the Kohn anomaly provides a means to predict $T_c$ of unknown materials and to estimate other key parameters such as coherence length and Fermi surface structure that link electronic and magnetic properties of these materials. This work predicts that Mg–Ba compounds with the AlB$_2$-type structure and BaB$_2$ will show superconducting properties. The approach used in this work amplifies the value of DFT computations as a predictive tool.

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References

52. A. Saengdeejing, PhD dissertation, Pennsylvania State University, 2011.