Identification of superconductivity mechanisms and prediction of new materials using Density Functional Theory (DFT) calculations

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Abstract. Superconductivity at room temperature or higher is considered a fundamentally viable goal, which may bring significant benefits to society, if achieved. However, methods to predict and design new superconductors remain largely empirical, without extensive guidance from computational quantum chemistry techniques, such as Density Functional Theory (DFT). This paper presents our progress, using DFT, towards a predictive tool for superconductivity from knowledge of the crystal structure. Excellent correlations between predicted and experimentally determined values have been demonstrated for MgB$_2$ under a wide range of external conditions, including isotopic forms, metal substitutions, pressure and temperature effects. Model ideas have recently been shown to work equally well for hydrogen sulphide (H$_3$S), which is the current record holder for the highest $T_c$ (at 200K), albeit requiring very high pressures (~160 GPa). Consistent patterns across families of superconductors, as determined from DFT calculations, are emerging that suggest a method to predict $T_c$ seems possible.

1. Introduction
Superconductivity at room temperature or higher is considered achievable by world experts [1] and remains an ultimate goal that may revolutionize the transport and storage of electricity with tremendous environmental benefits. However, approaches to design new superconducting materials remain largely empirical. Current theories, including those that make use of Density Functional Theory (DFT), predominantly explain properties post facto using additional formulae and corrections to match predictions to experimental values. Thus, the $ab\ initio$ merit of the DFT computation is largely destroyed.

The magnitude of the superconducting transition temperature, $T_c$, not only contributes to determine the practical applicability of the material (together with the critical current and the critical field), but also can help gain insight to the mechanisms and underlying interactions from which superconductivity emerges [2]. Based on the fact that the McMillan equation reasonably successfully determines $T_c$ from normal state parameters [3], we are led to believe that standard DFT may be capable of providing all the necessary superconducting characteristics of a material from knowledge of the crystal structure.

In this work, we present a summary of our progress towards the development of a predictive tool for superconductivity, as determined for hexagonal AlB$_2$-type structures, from the identification of anomalies in DFT calculated phonon dispersions (PDs). Highlights of our consistent extension of the approach to a different cubic structure case, that of hydrogen sulphide (H$_3$S), a superconductor at about
200K -- the temperature of a cold Antarctic day [4], are also presented.

2. Computational methods
All calculations are performed within the framework of first-principles DFT using the CASTEP module of Materials Studio 2017. LDA and GGA approximations are used as checks for consistency and a source for estimates of calculation errors [5-7]. Norm-conserving pseudo-potentials and density mixing schemes are used in the calculations. The electronic wave functions are expanded in terms of a plane-wave basis set with an energy cut-off of 990 eV. Other parameters are chosen to guarantee that the total energy convergence is within 1.0×10^{-6} eV atom^{-1}, maximum force at 0.01 eV Å^{-1}, maximum stress at 0.02 GPa and maximum atom displacement at 5×10^{-4} Å. The separation of k-points (Δk) is generally set to ≤ 0.03 Å^{-1}. Fine grids, increasing in fineness with the complexity of the structure, are required to resolve Fermi surface details and for reliable correlation between predicted and experimentally determined values within experimental error.

We measure the thermal energy δ given by the height or depth of the PD anomaly and calculate a corresponding temperature, T_δ, of the E_{2g} phonon(s) near the Γ zone centre, for each external condition, based on the following equation (1) (see Fig. 1) [5-7]:

\[ \delta = (nN/Z) \cdot (k_B T_\delta / 2) \] (1)

where δ 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_B T_δ / 2 is the well-known relationship between thermal energy and degrees of freedom.

3. Modelling results
Most results presented in summarized form here, have been collected over an extended period, and have been published in more detail in separate publications. Only highlights are given below.

3.1. Application to MgB_2 and other AlB_2-type structures
Using this approach, we have consistently correlated the PD anomalies associated with the E_{2g} phonon modes to the superconducting properties for MgB_2 and other related AlB_2-type structures [8], for the different isotopic forms of MgB_2 [9], for a series of substituted MgB_2 compositions with Al [5] and with transition metals [6] and for the pressure dependence of superconductivity in MgB_2 [7]. We have also used these ab-initio calculations to predict potential new superconductor materials with enhanced T_c [5-6]. Figure 1 below shows the definition of the PD anomaly depth or height, δ. Table 1 below summarizes the excellent correlation obtained between the calculated and published experimentally determined values of T_c, for which there is good synthesis and materials and property characterization work. The list would significantly increase if isotopic results, all other intermediate substitutions and determined values for the pressure dependence are tabled.

3.2. Temperature effects
More recently, temperature effects, simulated via frozen displaced atomic positions, have provided invaluable insight on the actual superconducting mechanism, give a potential explanation for the superconducting gap and confirm the correlation between PD anomalies and T_c [10]. The calculations for frozen, displaced atoms clearly show that the fraction of the highly covalent bond charge (or electron density), that responds to the atomic core attractions and repulsions as the atoms vibrate, produce the change in force constants responsible for the abrupt change in E_{2g} frequency. The depth of the PD anomaly corresponds to a critical amplitude of interatomic vibration before the energy of the E_{2g} mode (red) goes above the energy of the B_{1g} mode (blue) (see Fig. 1). These effects on the PDs coincide with the Fermi surface undergoing a topological transition. Topological transitions have more frequently been discussed in terms of variable composition [11]. However, according to our results, it would appear that concepts of analogous topological transitions may well apply to the influence of temperature effects.
Table 1. Comparison of DFT calculated and published experimentally determined $T_c$’s

| Compound                  | Predicted $T_c$ This work (K)$^*$ | Experimental $T_c$ By Others (K)$^+$ | References |
|---------------------------|-----------------------------------|-------------------------------------|------------|
| MgB$_2$                   | 42.0 (3.0)                        | 39.2 – 40.2                         | [8-9]** [15]|
| (Mg$_{0.8}$Al$_{0.2}$)B$_2$ | 31.3 (3.4)                        | 25 (2)–33.0 (0.1)                  | [5-6]** [16-17]|
| (Mg$_{0.66}$Al$_{0.34}$)B$_2$ | 16.2 (3.3)                        | 13.5 (0.1)                          | [5-6]** [16-17]|
| (Mg$_{0.8}$Al$_{0.2}$)B$_2$ | 4.6 (2.5)                         | 4.0 – 13.5                          | [5-6]** [16-17]|
| (Mg$_{0.86}$Sc$_{0.14}$)B$_2$ | 31.5 (4.4)                        | 23.0 (2.5)$^*$                      | [6]** [18-19]|
| (Mg$_{0.75}$Sc$_{0.25}$)B$_2$ | 11.4 (1.0)                        | 8.2 (5.0)$^*$                       | [6]** [18-19]|
| MgB$_2$(P=5 to 20 GPa)    | 49 – 19 (3.0)                     | 49 – 21                             | [7]** [20-21]|
| AlB$_2$                   | 0.0                               | 0.0                                 | [5-6]** [22]|
| BaSi$_2$                  | 9.3 (0.5)                         | 8.9                                 | [5-6]** [23]|
| Ca(Al$_{0.5}$Si$_{0.5}$)$_2$ | 7.5 (0.5)                         | 7.8                                 | [5-6]** [23]|

$^*$ $T_c$ for Sc substituted compositions were reported as the peak position of the derivative of the surface resistance, and since the transitions are about 8-10K broad, they shift the experimental $T_c$ by about 4-5K to lower values.

**References therein.

$^+$ Values in parentheses are one standard deviation.

The Fermi surface of MgB$_2$ consists of approximately parallel warped cylindrical sections [5,7]. As the atoms are displaced along the movement patterns of the $E_{2g}$ modes, at a critical relative displacement of ~ 0.6% (0.006 in relative coordinates), the light effective mass $\sigma$ Fermi surface cylinder collapses and can no longer participate in purely in-plane transfer of electrons and phonon generation with the heavy effective mass (that is without involvement of substantial $k_z$ components). The difference in Fermi energies at the equilibrium position and this critically displaced position correlates with the superconducting gap (see Fig. 2 below). MgB$_2$ offers a more straightforward correlation for this phenomenon, because charge transfers and atom displacements remain essentially in the same plane and directions up to and including the topological transition.
3.3. Hydrogen sulphide (H\textsubscript{3}S)

The recently discovered superconductor, hydrogen sulphide (H\textsubscript{3}S), is the current record holder for T\textsubscript{c} at about 200K, although it requires very high pressure (~ 160 GPa) to achieve this transition temperature which is equivalent to room temperature on a cold Antarctic day [4]. H\textsubscript{3}S has a cubic structure with Im-3m group symmetry [12]. Following the same modelling approach used for MgB\textsubscript{2}, we identify the phonon mode that is most strongly coupled to the electronic bands and/or electron density. Figure 3 displays a schematic of the H\textsubscript{3}S cubic structure at 200 GPa. The strongly electronic coupled, degenerate phonon modes are identified as the T\textsubscript{1u} modes, which involve stretching and contracting movements of the bond between a H in the centre of one of the cube faces (light blue) and S in the centre of the cube (yellow) (see Fig. 3).

Remarkably, critical relative displacements for the displaced atoms, which make the light effective mass electronic band lose its degeneracy at G and become tangential to the Fermi level, is in proportion to the respective T\textsubscript{c}'s, as are approximately the ratios of their differences in Fermi energies between the equilibrium and the relative, critically displaced atomic positions (0.03 and 0.006 for H\textsubscript{3}S and MgB\textsubscript{2}, in relative coordinates, respectively).

4. Discussion

A significant part of the work presented here follows the early lead from An and Pickett [13] on deformation potentials created by the displacement of boron atoms along the E\textsubscript{2g} mode, which stretches and contracts the inter-bond distance. Notice that the difference in Fermi energies at the equilibrium position and at the critical displacement of about 0.6% (0.006 in relative coordinates) is about twice the superconducting gap energy for MgB\textsubscript{2}.

**Figure 2.** Variation of the Fermi energy of MgB\textsubscript{2} as function of the relative displacement of the B-B atom positions along the E\textsubscript{2g} mode, which stretches and contracts the inter-bond distance. Notice that the difference in Fermi energies at the equilibrium position and at the critical displacement of about 0.6% (0.006 in relative coordinates) is about twice the superconducting gap energy for MgB\textsubscript{2}.

\[
E_F = \frac{\hbar^2}{2m_e} \left(3\pi^2 n\right)^{2/3}
\]

\[
E_F \approx 17.5 \text{ meV}
\]

\[
E_{F_{\text{tang}}} - E_{F_{\text{equil}}} = 2\Delta
\]
energy gaps are established. It is thus the interplay between the heavy and light effective mass Fermi surfaces (and the volume in between), which appears to control $T_c$.

The $E_{2g}$ modes are strongly coupled to the electron density and are the most affected by variation in external conditions such as pressure, isotopic effects and elemental substitutions. Similarly, a degenerate $T_{1u}$ mode in $H_3S$ has been identified as strongly coupled to the electron density and the most responsive to variations in external conditions. Regular, consistent patterns in the characteristics of superconductors, as determined from standard DFT calculations of electronic bands, phonon dispersions and the effects of frozen displaced atomic positions, particularly if they follow key phonon modes, are becoming understood.

Given the growing list of examples [5-10, 14], which are producing excellent matches between calculated values of $T_c$ and well determined experimental values, we posit that a method to determine $T_c$ from a knowledge of the crystal structure is now emerging.

5. Conclusions
Consistent examples of accurate determinations of $T_c$ for $\text{MgB}_2$ and other related $\text{AlB}_2$-type structures under a range of external conditions have been provided. This approach has also been validated for other crystal structures. Thus, standard DFT calculations can provide direct information about superconductivity of compounds from a knowledge of the crystal structure without requiring post calculation corrections or parameter adjustments. Identification of consistent patterns of properties across families of superconductors, as determined from DFT calculations, indicate that a potential tool for prediction of superconductivity is emerging.

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