

CONCENTRATION DEPENDENCE OF SUPERCONDUCTING STATE PARAMETER: A *FIRST PRINCIPLE STUDY*

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ABSTRACT

In the present manuscript the concentration dependent study of superconducting state parameters viz., Coulomb pseudopotential μ^* , electron – phonon coupling strength λ , SC transition temperature T_C , interaction strength N_0V , semi band gap Δ , energy or mass renormalization parameter Z_0 and isotope effect exponent δ have been studied. Harrison's First Principle pseudopotential (HFPP) technique in conjunction with BCS theory and McMillan's formalism has been used in the present investigation. Reasonable agreement with theoretical and experimental data has been obtained.

KEYWORDS: BCS theory, Superconductivity, Diboride.

1. INTRODUCTION

The discovery of superconductivity in diboride material (MgB_2)^[1] was serendipitous and sparked considerable interest in this class of material.^[2,3] A lot of research is being carried out in order to understand the mechanism and study its associated properties as borides based material are found to be promising candidate for generating high magnetic fields and as superconducting cables. In order to meet future energy demands, the transmission capacity of cable are suppose to be increased and in this direction this class of material appear to be a promising material. Being cheaper and simple material to use, the superconducting cables made up of diboride material like MgB_2 can be easily fabricated into wires and can be used for high current applications. Due to its large coherence length, high critical current densities is achievable in this type of material.^[4] By studying the isotope effect on the critical

temperature and critical field of superconductors, the information about the interaction resulting in superconductivity can be revealed. Several attempts have been made in the past to study the critical temperature dependence on various parameters like pressure, volume and other several factors.^[5-13] but hardly any attempt has been made to study concentration dependence of critical temperature and other associated properties. The material aluminum diboride also belong to this class of material and is a combination of metal and semi metal. The material aluminium diboride (AlB_2) was first prepared by Funk.^[14] and the first XRD analysis was carried out by Hofmann and Jamiche.^[15] Since then various theoretical attempts have been made to explain its superconducting behavior and also to compute its superconducting transition temperatures.^[3-9,16-23] However, it has been suggested that the BCS theory may be applied to this system safely.^[10,24]

In the present work, the theoretical investigation of SC (superconducting) state transition parameters of this system (AlB_2) assuming the validity of BCS theory, Pseudopotential formalism and the Faber-Ziman formalism for the computation of the form – factor of AlB_2 and consequently the McMillan's formula for the computation of SC state transition temperature. An overall reasonable agreement has been obtained for various SC state parameters and the band gap has also been satisfactorily reproduced. The formation of complexes in liquid alloys has encouraged us to use the Faber – Ziman formalism for the computation of form-factor of the system AlB_2 from the form-factors of the constituents.

The form factor has been calculated with two sets of core energy eigenvalues viz., those of Herman – Skillman,^[19] and Clementi,^[20] represented by H and C respectively.

An attempt has been made to introduce a parameter α in the conduction band core exchange potential v_q^c , on the lines of Kohn and Sham ($\alpha = \frac{2}{3}$) based on variational principles and ($\alpha = \alpha_{v.}$) Virial theorem by Schwarz.^[20] Both these have been attempted.

In the potential V_{OPW} two values orthogonalization hole parameter β has been used $\beta = 1$ and $\beta = \frac{5}{8}$ on the lines of Harrison.^[18] The potential v_{OPW} which is involved in the screening potential, energy dependent components and the repulsive potential via the core shift f_{nl} .

In order to calculate form factor, V-S,^[22] form of exchange – correlation has been employed as it satisfies the compressibility rule and provides clear picture of interionic pair potential.

In the following sections, the formalism of the non – local screened form factor and also that of other SC state parameters are presented. The SC properties like Coulomb pseudopotential μ^* , electron – phonon coupling strength λ , SC state transition temperature T_C , the mass or energy renormalization parameter Z_0 , the effective interaction strength $N(0)V$, the isotope effect exponent δ are calculated.

2. Formalism and Computation

2.1 Form Factor

Form Factor is the Fourier transform of the crystal potential in the reciprocal lattice. It is the potential dependent term and algebraic sum of the following interacting potentials.

- (i) Effective valence charge and core electron potential, v_{ab}^*
- (ii) Effective conduction band core exchange potential, v_c^*
- (iii) Effective conduction electron potential, v_d^*
- (iv) Effective screening potential, v_f^*
- (v) Repulsive potential, W^R

The energy dependent components are the repulsive potential W^R and screening potential v_q^f where the *energy independent components* which do not involve core energy eigenvalues ε_{nl} are

- (i) The valence charge and core electron potential, $v_q^{a,b}$
- (ii) The conduction band core exchange potential, v_q^c
- (iii) The single OPW, conduction electron potential, v_q^d

Which when considered together are termed as *bare ionic potential* v_q^0 . It consists of the following

(a) **The valence charge potential** is the potential arising from the net core charge equal to the valency of the metal and is simply $-Ze^2/r$ where Z is the valency and e is the electronic charge. It is given by

$$v_q^a = -\frac{8\pi Z}{\Omega_0 q^2} \quad (1)$$

where $\Omega_0 = \Omega/N = \text{Atomic volume}$. All energies are in rydberg, distances in Bohr radii, wave numbers in reciprocal Bohr radii and all quantities in atomic units (a.u.).

(b) The core potential is the coulomb potential arising from the remainder of the nuclear and expressed as

$$v_q^b = -\frac{8\pi Z}{\Omega_0 q^2} [n(r) - n(0)] \quad (2)$$

where,

$$n(r) = \text{core electron density} = \frac{\sum_{nl} 2(2l+1)P_{nl}^2(r)}{4\pi r^2}$$

$$n(0) = \text{number of core electrons} = \sum_{nl} 2(2l+1)$$

Where $P_{nl}(r)$ is the normalized radial wave function; n and l are the total and angular quantum numbers respectively when considered together they form a neutral core and thus the potential is localized to the core region. They are termed as valence charge and core electron potential v_q^{ab} .

$$\therefore v_q^{ab} = v_q^a + v_q^b = -\frac{8\pi Z}{\Omega_0 q^2} [-Z - n(0) - n(r)] \quad (3)$$

(c) The conduction band core exchange potential: This is the exchange interaction between the conduction and core electrons and is included through the Slater's $X\alpha$ -exchange. It is expressed as

$$v_q^c = -6\alpha \left(\frac{3}{8\pi}\right)^{1/3} \left(\frac{4\pi}{\Omega_0 q}\right) \int (\sin qr)(r(U(r)))^{1/3} dr \quad (4)$$

Here, α is the conduction band core exchange parameter.

(d) The conduction electron potential: It is defined as the potential due to charge density of the single and unnormalized OPW states. Due to the normalization, the probability density gives rise to an orthogonalization hole electron density. The orthogonalization hole assumed to be distributed as the charge as the charge of core electron and is expressed as

$$v_q^d = -\frac{8\pi Z}{\Omega_0 q^2} \frac{n(r)}{n(0)} \left(\frac{Z^*}{Z} - 1 \right) \quad (5)$$

Based on this, the energy independent components which are the algebraic sum of the Fourier transform of the above mentioned potential can be obtained as:

$$N \langle \mathbf{k} + \mathbf{q} | V(r) | \mathbf{k} \rangle = v_q^{ab} + v_q^c + v_q^d = v_q^0 \quad (6)$$

This is also known as the Bare – ionic potential.

Apart from it there are several energy dependent components like:

(a) The repulsive potential is the only repulsive component of the form factor and it comprises the core energy eigenvalues. It is expressed as:

$$\begin{aligned} W^R &= \langle \mathbf{k} + \mathbf{q} | W^R | \mathbf{k} \rangle \\ \Rightarrow W^R &= \sum_{nl} (k^2 + f_{nl}) (2l+1) \langle \mathbf{k} + \mathbf{q} | nlo \rangle \langle \mathbf{k} | nlo \rangle P_l(\cos \theta) \\ &+ \frac{\sum_{nl} (k^2 + f_{nl}) (2l+1) \langle \mathbf{k} | nlo \rangle^2}{1 - \sum_{nl} (2l+1) \langle \mathbf{k} | nlo \rangle^2} \times \frac{\sum_{nl} (k^2 + f_{nl}) (2l+1) \langle \mathbf{k} | nlo \rangle^2}{1 - \sum_{nl} (2l+1) \langle \mathbf{k} | nlo \rangle^2} \\ &\quad \times \left[\sum_{nl} (2l+1) \langle \mathbf{k} + \mathbf{q} | nlo \rangle \langle \mathbf{k} | nlo \rangle P_l(\cos \theta) \right] \end{aligned} \quad (7)$$

Where,

$$f_{nl} = -3.6 \frac{Z^*}{r_0} + v_0^b + v_0^c + |\epsilon_{nl}| - V_{OPW},$$

is the core shift that represents the shift in the Hartree energies due to various interacting potentials.

Here, the symbol ‘o’ with nl stands for magnetic quantum number $m = 0$.

$$\langle \mathbf{k} | nlo \rangle = \left(\frac{4\pi}{\Omega_0} \right)^{1/2} \int r P_{nl}(r) j_l(kr) dr$$

$$\langle \mathbf{k} + \mathbf{q} | nlo \rangle = \left(\frac{4\pi}{\Omega_0} \right)^{1/2} \int r P_{nl}(r) j_l(|\mathbf{k} + \mathbf{q}|r) dr$$

$$r_o = \text{radius of the atomic sphere given by } \left(\frac{3\Omega_0}{4\pi} \right)^{1/3}$$

(b) **The screening potential** is the interaction between the conduction electrons among themselves and is responsible for the screening of the form factor. The screening potential is given by

$$v_q^f = \frac{4}{\pi k_F \eta^3} \int_{-1}^{+1} \frac{dZ}{\eta + 2Z} \int_0^{(1-Z^2)^{1/2}} d\rho 2\rho \langle \mathbf{k} + \mathbf{q} | W^R | \mathbf{k} \rangle \quad (8)$$

The non-local screened form factor may be expressed as,

$$\begin{aligned} w(\mathbf{k}, \mathbf{q}) &= v_{ab}^* + v_c^* + v_d^* + v_f^* + W^R \\ &= v_0^* + v_f^* + W^R \end{aligned} \quad (9)$$

Where, $v_0^* = v_{ab}^* + v_c^* + v_d^*$

$$v_{ab}^* = \frac{v_q^{ab}}{\varepsilon^*(q)}; \quad v_c^* = \frac{v_q^c}{\varepsilon^*(q)}; \quad v_d^* = \frac{v_q^d}{\varepsilon^*(q)}; \quad v_f^* = \frac{v_q^f}{\varepsilon^*(q)}$$

And $W^R = \langle \mathbf{k} + \mathbf{q} | W^R | \mathbf{k} \rangle$

Due to the contribution of valence electrons, the bare-ionic potential $w^0(\mathbf{k}, \mathbf{q})$ gets modified. This process is termed as screening of the form-factor and it arises from the exchange-correlation motion of electron being accommodated through exchange-correlation function $G(q)$ or $G(\eta)$. There are various exchange and correlation functions $\varepsilon^*(q)$ like Hubbard – Sham (H-S),^[23] Kleinmann – Langreth (K-L),^[24] and Shaw,^[25] form of screening used by many researchers. The V-S exchange,^[22] satisfies the compressibility sum rule.

Vashishta – Singwi (V- S) Exchange and Correlation function

Singwi and his co-researchers in a series of papers,^[26,27] have discussed the problem of exchange and correlation to Hartree dielectric function and it help in obtaining $G(q)$ in a self – consistent manner thereby relating it with pair correlation function. In the final theory given by Vashishta – Singwi,^[22] based on research of Singwi *et al.*,^[26,27] the change in the pair correlation function is incorporated. In case of metallic densities, the self consistent value of $G(\eta)$ is expressed as

$$G(\eta) = A(1 - e^{-B\eta^2}) \quad (10)$$

Which is valid only for $\eta \leq 2$ where $\eta = \frac{q}{k_F}$, the constants A and B satisfies the compressibility rule and are dependent on the Wigner – Seitz sphere radius.

The pseudopotential form factor and other parameters of the binary system may be calculated based on Vegard's law as,

$$X_{AB} = (1-c)X_A + cX_B \quad (11)$$

Where, X_A and X_B are the parameters or form factor of the constituents and X_{AB} those of the binary system, c is the concentration of the second constituent.^[28]

The Debye temperature (θ_D) of the binary system can be represented by.^[29]

$$\frac{1}{(\theta_D)_{AB}^2} = \frac{1-c}{(\theta_D)_A^2} + \frac{c}{(\theta_D)_B^2} \quad (12)$$

The SC parameters can be calculated through the well established McMillan's formalism.^[30]

The electron – phonon coupling strength is given by

$$\lambda = \frac{12m^*Z^*}{M\langle\omega^2\rangle} \int_0^1 \eta^3 |w(\mathbf{k}, \mathbf{q})|^2 d\eta \quad (13)$$

where m^* is the effective mass of the electron, Z^* the effective valence, M the atomic mass, $\langle\omega^2\rangle$ the averaged phonon frequency and $\eta = q/2k_F$.

The Coulomb pseudopotential is represented by

$$\mu^* = \frac{\left[\frac{m_b}{\pi k_F} \right] I}{\left[1 + \frac{m_b}{(\pi k_F)} \ln \left(\frac{E_F}{K_B \theta_D} \right) \right] I} \quad (14)$$

$$\text{With } I = \int_0^1 \frac{d\eta}{\eta \varepsilon^*(\eta)} \quad (15)$$

Where, m_b is the band mass, E_F the Fermi energy, K_B the Boltzmann constant, θ_D the Debye temperature and k_F the Fermi wave vector. The Superconducting transition temperature is given by

$$T_C = \frac{\theta_D}{1.45} \exp \left\{ \frac{-1.04(1+\lambda)}{(\lambda - \mu^*(1+0.62\lambda))} \right\} \quad (16)$$

The energy renormalization parameter is given by

$$Z_0 = \left[1 + \frac{10}{11} \lambda \right] \quad (17)$$

The effective interaction strength is given by

$$N(0)V = \frac{[\lambda - \mu^*]}{1 + \frac{10}{11}\lambda} \tag{18}$$

The isotope effect exponent is given by

$$\delta = \frac{1}{2} \left[1 - \left\{ \mu^* \ln \left(\frac{\theta_D}{1.45T_C} \right) \right\}^2 \frac{1 + 0.62\lambda}{1.04(1 + \lambda)} \right] \tag{19}$$

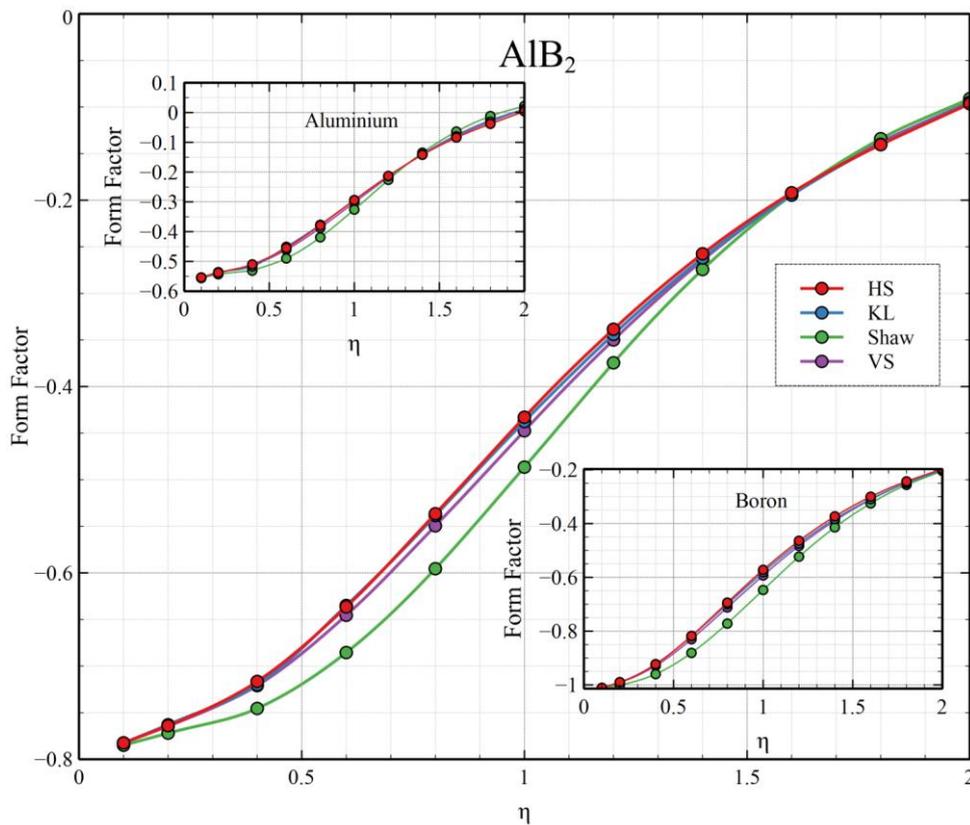


Fig. 1

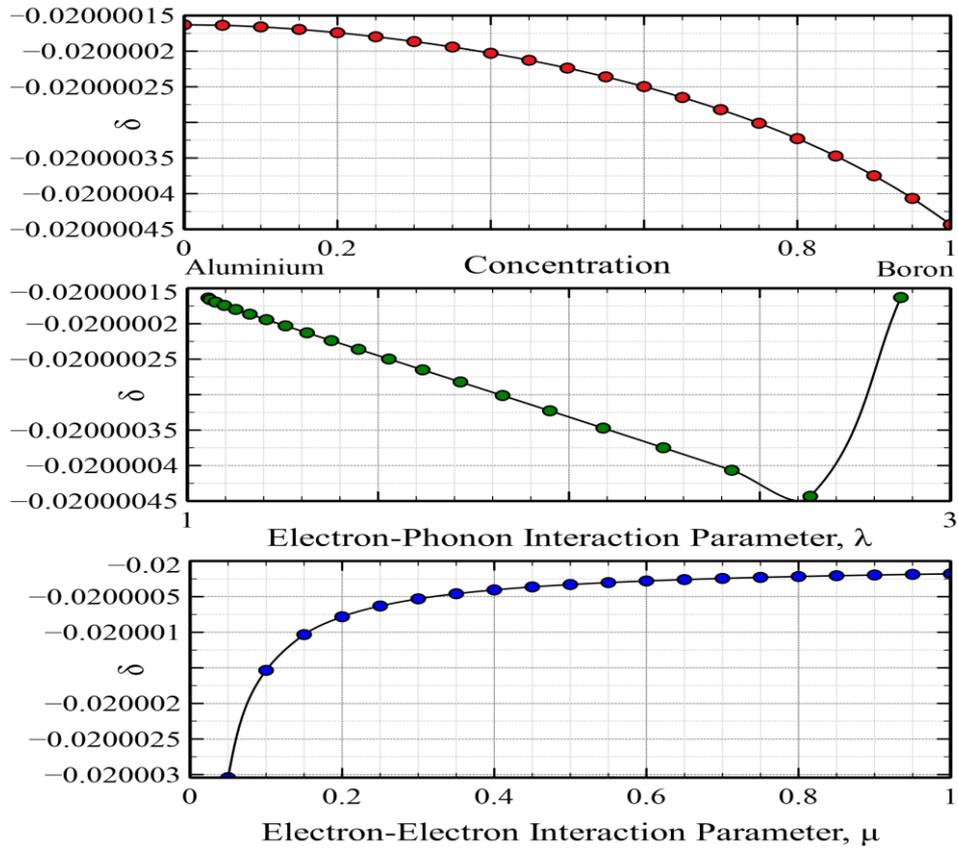


Fig. 2

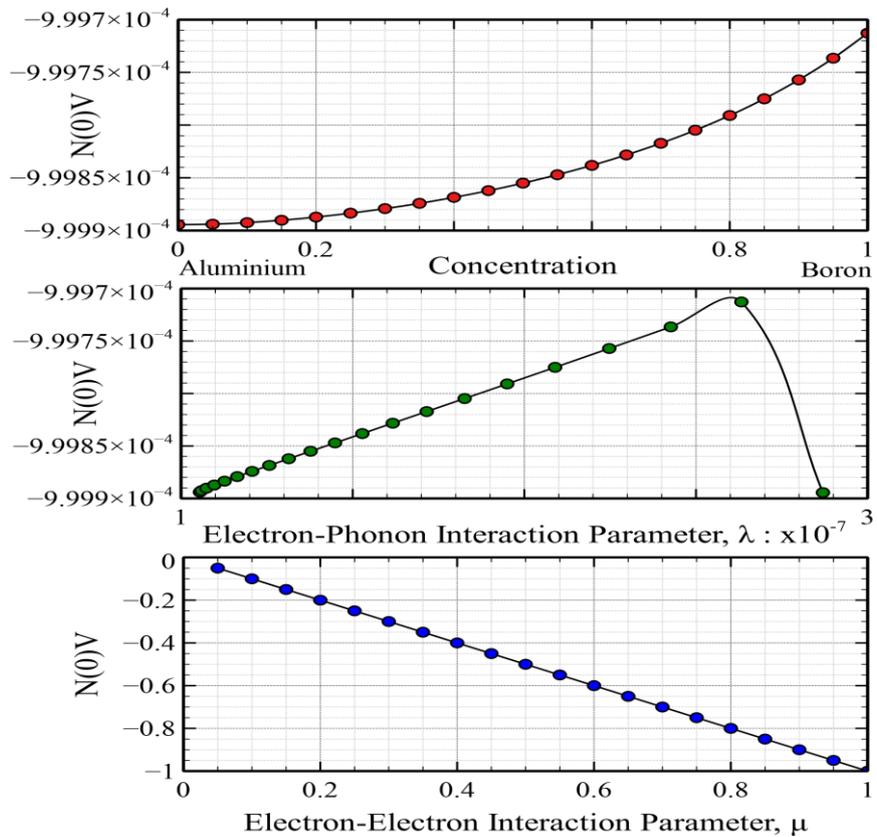


Fig. 3

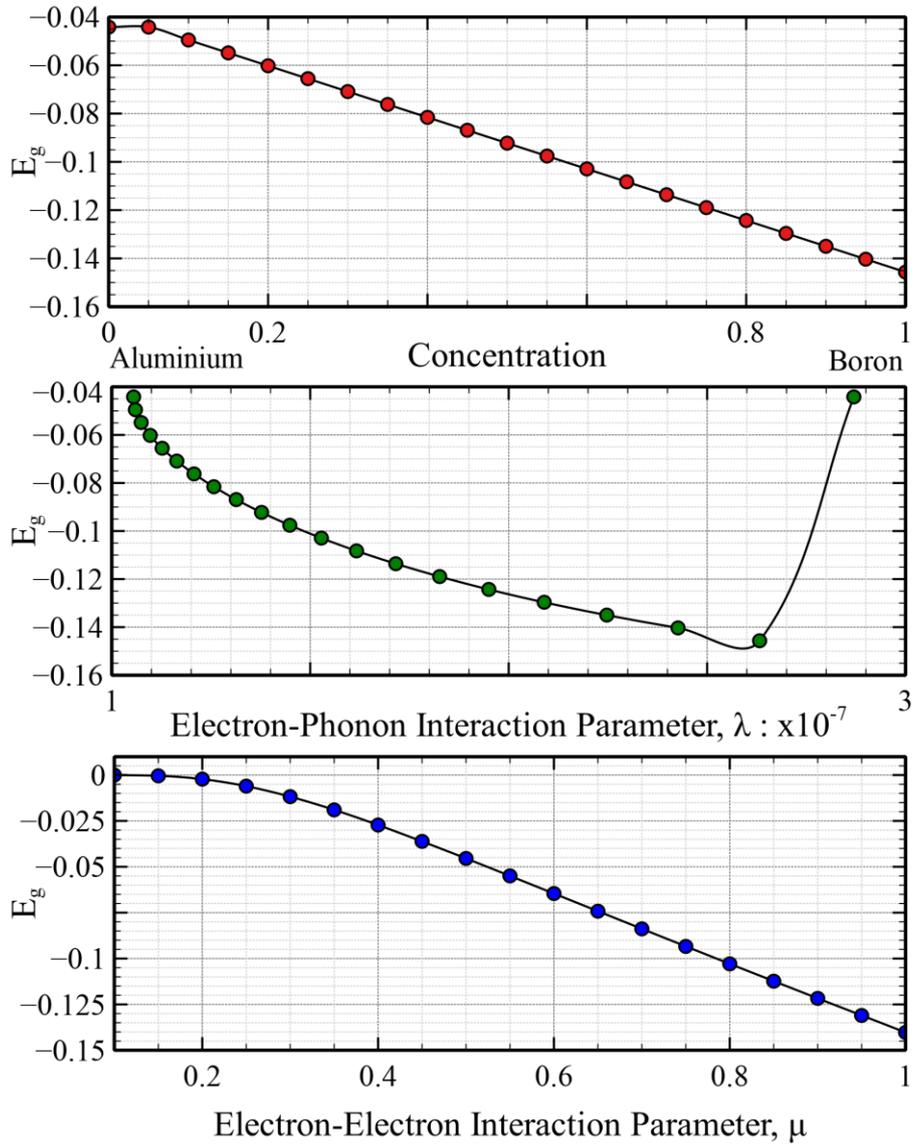


Fig. 4

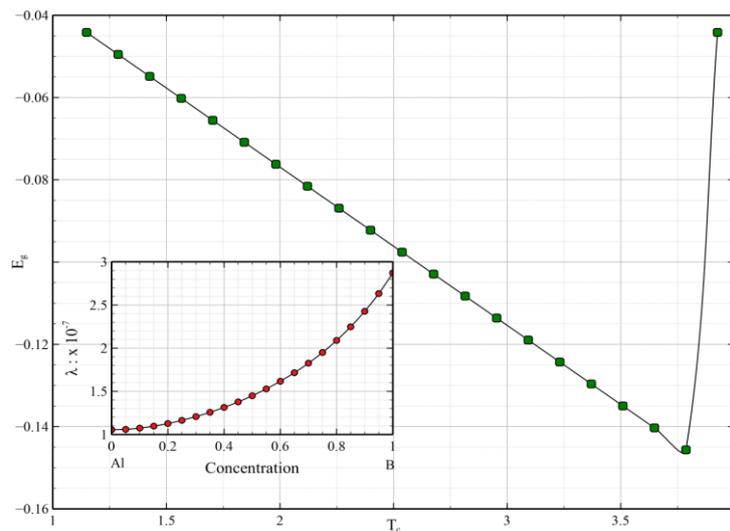


Fig. 5:

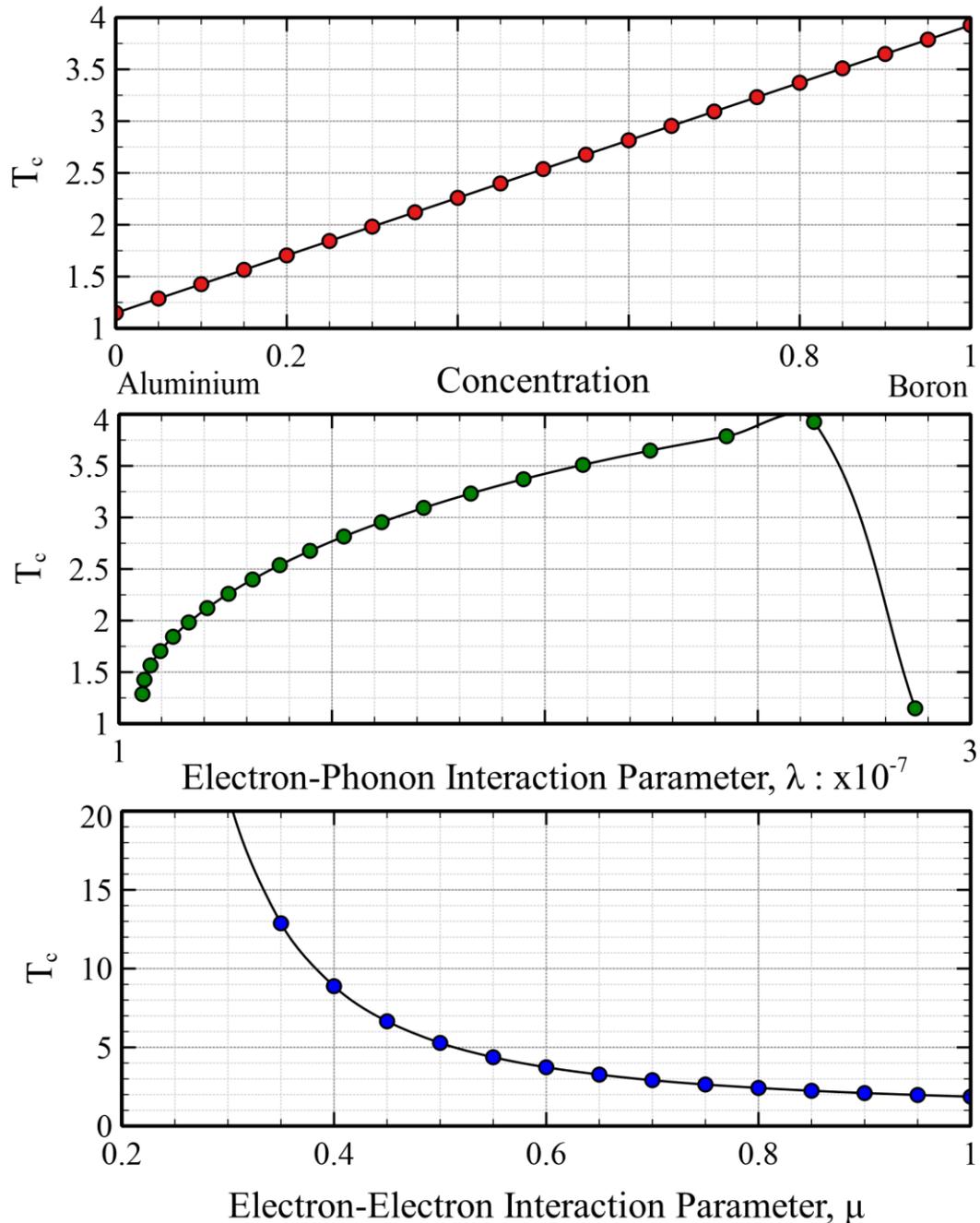


Fig. 6

3. RESULTS AND DISCUSSION

The computed form factor $w(\mathbf{k}, \mathbf{q})$ of AlB_2 have been presented in **Fig. 1** which provide reasonable values of the electron – phonon coupling strength λ and the SC transition temperature T_c . From figure it is clear that that of the boron atom dominates the form factor of AlB_2 . This implies that B – atoms in the boron layers play more significant role as observed by Singh,^[30] through band structure calculations.

It is known that at ambient conditions AlB_2 crystallizes in hp-3 structure where B – atoms form honeycomb lattice consisting of graphite like sheets separated by hexagonal layers of Al atoms. Moreover single crystals of AlB_2 exhibits metallic conductivity along the axis parallel to the basal hexagonal plane,^[34] The pairing mechanism leading to SC is of phononic origin. Thus the B – atoms plays dominant role in shaping the form factor. It is observed that the most contributing part of the form factor $w(\mathbf{k},\mathbf{q})$ is in the region $1 \leq \eta \leq 2$ where $\eta = q / k_F$. This is because the integrand involves the η^3 and $|w(\mathbf{k},\mathbf{q})|^2$ like the Ziman integrand for electrical resistivity.

Since the value of μ^* , is a poorly known quantity, it is varied from 0 to 1 and it is found that a higher T_c can be obtained at low values of μ^* (Fig. 2). It is observed that effective interaction strength, $N(0)V$ (Fig. 3) falls linearly when this parameter (μ^*) is increased. Further the isotope effect exponent, δ saturates with the increase in μ^* .

The electron-phonon coupling parameter, λ represents quadratic behavior with second order polynomial relationship with the concentration gradient of the elements Al and B forming the alloy AlB_2 . When this parameter is analysed with respect to effective interaction strength, $N(0)V$ it attains maximum value whereas isotope effect exponent, δ attains minimum value when varied with respect to λ suggesting formation of stable superconducting phase. Evaluation of λ through electronic specific heat coefficient γ is given as

$$\lambda = \gamma_{\text{exp.}} / \gamma_{\text{calc.}} - 1 \quad (20)$$

$$\text{Where, } \lambda_{\text{calc.}} = 1 / 3 \pi^2 D (E_F) k_B^2 \quad (21)$$

The suitable form factors $w(\mathbf{k},\mathbf{q})$ have been identified and they have been used to compute other SC state parameter viz, mass or energy renormalization parameter Z_0 , effective interaction strength $N(0)V$ and the isotope effect exponent δ .

The band gap $E_g=2 \Delta(0)$ has been calculated as

$$\Delta(0) = \frac{k_B \theta_D}{\text{Sin h} \left[\frac{1}{N(0)V} \right]} \quad (22)$$

Where

$$\frac{1}{N(0)V} = \ln \frac{1.14\theta_D}{T_c} \quad (23)$$

It is found that value of energy gap decreases (**Fig. 4, Fig. 5**) and almost vanishes at superconducting T_c . It is observed that the net electron-electron becomes attractive and all electrons are coupled to form cooper pairs in the ground state. The paired electrons are repeatedly scattered between single electron state.

Thus λ and T_c (**Fig. 6**) computed through form factors using various input parameters have also satisfactorily reproduced the other SC state parameters Z_0 , N_0V and the band gap Δ .

4. CONCLUSION

The HFPP technique has been successfully implemented in conjunction with BCS theory to study the various properties of AlB_2 inherent in the superconducting state. It is found that B – atoms in the boron layers play more significant role as observed by Singh^[30] through band structure calculations. Moreover, AlB_2 crystallizes in hp-3 structure where B – atoms form honeycomb lattice consisting of graphite like sheets separated by hexagonal layers of Al atoms. It is observed that the most contributing part of the form factor $w(\mathbf{k},\mathbf{q})$ due to Boron atoms in the region $1 \leq \eta \leq 2$ where $\eta = q / k_F$. Higher value of T_c can be obtained at low values of μ^* . It is found that the electron-phonon coupling parameter, λ behaves quadratically with second order polynomial relationship with the concentration gradient of the elements Al and B forming the alloy AlB_2 . The energy gap decreases and almost vanishes at superconducting T_c . It is observed that the net electron-electron becomes attractive and all electrons are coupled to form cooper pairs in the ground state. The pairing mechanism leading to SC is of phononic origin.

Superconducting Parameter of the superconductor AlB_2 having double layered structure where boron atoms form honeycomb lattice separated by hexagonal layers of Al atoms. Superconductivity mainly arises due to Boron. There is a flat band in the vicinity of the Fermi level and the B atoms are involved in electron-phonon coupling in the system.

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