Elastic behavior, pressure-induced doping and superconducting transition temperature of GdBa$_2$Cu$_3$O$_{7-x}$

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Abstract
Doping superconductors are known to vary the superconducting transition temperature $T_c$, depending on the degree of holes or electrons introduced in a system. In this study, we report how pressure-induced hole doping influences the $T_c$ of GdBa$_2$Cu$_3$O$_{7-x}$ superconducting perovskite. The study was carried out in the framework of density functional theory (DFT) using the Quantum espresso code. Ultrasoft pseudopotential with generalized gradient approximation (GGA) functional was used to calculate the ground state energy using the plane waves (PW). The stability criterion was satisfied from the calculated elastic constants. The BCS theory and the Mc Millan’s equation was used to calculate the $T_c$ of the material at different conditions of pressure. The underdoped regime where the holes were less than those at optimal doping was found to be below 20 GPa of doping pressure. Optimal doping where the material achieved the highest $T_c$ (max) $\sim$ 20 GPa of the doping pressure. Beyond the pressure of $\sim$20 GPa was the over doping regime where a decrease in $T_c$ was recorded. The highest calculated $T_c$ (max) was $\sim$141.16 K. The results suggest that pressure of $\sim$20 GPa gave rise to the highest $T_c$ in the study.

1. Introduction

Superconductors are among the materials that have attracted more attention in research because of the projected benefits they can deliver if better and efficient ones are discovered [1,2]. This has motivated researchers and industrial users to improve the electronic structure and mechanical properties to achieve the conditions for better performance. One of the ways that have been applied is doping to vary the number of holes and electrons in the crystals of the material to affect the electronic charge behavior of a material, and the structure at the Fermi level [3,4]. Both theoretical and experimental methods have been embraced to achieve new discoveries in these efforts. The superconducting environment and other associated material properties greatly affect the performance of the superconductor towards realizing efficiency. Elastic behavior of materials is a true measure of how material deformations relate to external stress [3]. The behavior is more important in determining how best materials can change due to intrinsic and extrinsic effects that affect the atomic orientation and structural geometry. This change is much dependent on the chemical composition, the structure of the crystal lattice, and the deforming stress. Under pressure, a material undergoes several elastic behavior changes due to the reduction of interatomic orbitals which modifies the electronic orbitals and the order of bonding. If the structure remains unaffected by the loading stress, the electronic properties get highly modified. Some of these modifications include; broadening of the bandgap, change of the Fermi energy, induction of semiconductor to conductor change, and change of ordering of the electronic states. When the cuprate superconductors undergo doping, their normal state behaves as an ordinary Fermi liquid similar to metals and the superconducting properties can thus be described by the Bardeen-Cooper-Schrieffer (BCS) theory [6–7].
The strength of a material can be explained based on phonons in a crystal lattice. These vibration modes decrease the forces acting on the displaced atoms from the equilibrium position symmetry. As a result, the frequency of their oscillation is also decreased. The effect leads to lattice distortions which are periodic in nature and as a result, the energy of the crystal is lowered and makes the distribution of energy to the soft phonons to be negative. In this case, the criterion for the crystal stability will be associated with the phonon frequencies; and depending on its magnitude, instability can occur. Since the Debye temperature is related to phonon frequency, its magnitude also has the same effect. In this study, the Elastic properties of Doped GdBa₂Cu₃O₇−ₓ at different pressures are used to calculate the Debye constant from which the superconducting transition temperature is calculated. The material undergoes polymorphic phase transition in which the stable orthorhombic phase changes to unstable tetragonal phase when subjected to a pressure of ~21 GPa and thus above that pressure the stability criterion of the orthorhombic phase may not be satisfied since the material undergoes distortion [8]. The paper will continue in the order: section 2, computational methods; section 3, results and discussion, and section 4, conclusion.

2. Computation methods

The first principle calculations for this study of GdBa₂Cu₃O₇−ₓ under induced-pressure doping was undertaken in the framework of density functional theory (DFT) based on plane wave self-consistent field (PWscf) and ultra-soft pseudopotential (USPP) method as treated in the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation and local density approximation. The computational calculations were performed using the Quantum Espresso simulation package. Optimized cell dimensions, the k-points, and the kinetic energy cut-off values were properly checked through graphing and accurate values were obtained at the convergence of the ground state energy at minimum convergence threshold in the calculation using the proper basis sets. The optimization was thought to have been achieved by considering the volume at minimum energy in the pressure-volume graph and energy volume graph using the Birch Murnaghan equation fitting. The valence configuration used for GdBa₂Cu₃O₇−ₓ was 4f⁷5d¹6s² for Gadolinium, 6s² for Barium, 3d¹⁰4s¹ for Copper and 2s²2p⁴, for Oxygen. The convergence threshold used was 10⁻⁶eV which is sound for accuracy. The Brillouin sampling was based on the Monkhost scheme [9]. The K-point mesh in the irreducible high symmetry points in the Brillouin zone used was 6 × 6 × 2. For the elastic constant calculation, the ‘quasi-static approximation was used where the elastic constants were computed at zero absolute temperature and saved as elastic constants. This means that quantum espresso code interpolated the elastic constants and the energy that minimizes the Helmholtz free energy at a specific temperature. The superconducting transition temperature was based on Mc Millan equation of superconducting transition temperature developed from Eilenberg theory and given by [10]:

\[ T_c = \frac{\theta_D}{1.45} \exp \left[ \frac{-1.04(1 + \lambda)}{\lambda - \mu^\ast(1 + 0.62\lambda)} \right] \]  

(1)

Where \( \theta_D \) is the Debye temperature, \( \mu^\ast \) is the renormalized Coulomb repulsion and its value is chosen to range from 0.1–0.2 [11,12] and \( \lambda \) is the electron-phonon coupling constant. The application of BCS theory in the calculation of superconducting transition temperature for cuprate superconductors (GdBa₂Cu₃O₇−ₓ) requires doping and this was achieved through pressure induction.

3. Results and discussions

In this section, we present the results for the computed structural parameters; elastic constants; the Debye temperature, and calculated values of the superconducting transition temperature for GdBa₂Cu₃O₇−ₓ. The results are discussed in relation to how the stability and pressure doping affect the superconducting transition temperature of the material.

3.1. Structural parameters

The optimized lattice parameters under different conditions of pressure are presented in (table 1). The lattice parameters in the \( a \), \( b \) and \( c \) directions reduce with increased pressure. The space group of the material below the pressure of 20 GPa is Pmmm (orthorhombic phase) while above ~20 GPa the space group is P4/mmm (tetragonal phase).
3.2. Elastic properties

The elastic constant is the basic parameter in the study of how materials respond to stress and from which all other mechanical properties can be calculated. The constant determines the anisotropic and isotropic stability of a material\[13,14\]. By application of the non-volume conserving approach, the deformations resulting from the displacement of the primitive cell from their equilibrium position were used to determine the elastic tensor, and thus the elastic constant was found as\[15\]:

\[ s_{ij} = \frac{\partial \epsilon_{ij}}{\partial \sigma_{kl}} \]

Where \( \sigma_{ij} \) and \( \epsilon_{ij} \) are the applied stress and the Eulerian strain tensors respectively.

The orthorhombic crystal for the GdBa\(_2\)Cu\(_3\)O\(_7\)-\(x\) has nine independent constants: \( C_{11}, C_{22}, C_{33}, C_{12}, C_{13}, C_{23}, C_{44}, C_{55}, \) and \( C_{66} \)[16,17]. The constants \( C_{ij} \) (table 2) were used to calculate the elastic moduli, shear moduli, and bulk moduli and are presented as a function of pressure as shown in the table 3 below.

The mechanical stability criteria for the orthorhombic phase of GdBa\(_2\)Cu\(_3\)O\(_7\)-\(x\) under zero pressure and the isotropic condition is satisfied by the following conditions [16,17].

### Table 1. Calculated lattice parameters (a, b, c in Å) of GdBa\(_2\)Cu\(_3\)O\(_7\) under pressure up to 40 GPa.

| \( P \) (GPa) | \( a \) (Å) | \( b \) (Å) | \( c \) (Å) |
|--------------|--------------|--------------|--------------|
| 0            | 3.8482       | 3.9481       | 11.7023      |
| 5            | 3.8381       | 3.9300       | 11.6368      |
| 10           | 3.8281       | 3.9161       | 11.4306      |
| 15           | 3.8190       | 3.9030       | 11.3846      |
| 20           | 3.8101       | 3.8863       | 11.3542      |
| 25           | 3.8026       | 3.8711       | 11.3358      |
| 30           | 13.10        | 403.35       | 3154.52      |
| 35           | 15.33        | 334.54       | 2451.43      |
| 40           | 18.54        | 225.10       | 1579.71      |

### Table 2. Calculated elastic constants \( C_{ij} \) (GPa) of GdBa\(_2\)Cu\(_3\)O\(_7\)-\(x\) under pressure up to 25 (GPa). For \( C_{ii} \) (i = 1, 2, 3, 4, 5, 6) the elastic constant increases with pressure as opposed to \( C_{ij} \) (\( i \neq j \)).

| \( P \) (GPa) | \( C_{11} \) | \( C_{22} \) | \( C_{33} \) | \( C_{12} \) | \( C_{13} \) | \( C_{23} \) | \( C_{14} \) | \( C_{25} \) | \( C_{66} \) |
|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| 0            | 125.15       | 126.73       | 115.86       | 80.41        | 38.22        | 42.94        | 39.68        | 27.84        | 57.31        |
| 5            | 180.35       | 207.34       | 154.64       | 89.02        | 51.61        | 52.67        | 48.04        | 34.97        | 67.39        |
| 10           | 225.16       | 270.89       | 217.71       | 115.12       | 76.63        | 217.71       | 53.19        | 42.09        | 76.61        |
| 15           | 256.14       | 318.62       | 229.03       | 132.31       | 89.83        | 86.10        | 57.35        | 46.87        | 81.91        |
| 20           | 287.13       | 354.79       | 240.12       | 149.23       | 102.45       | 96.20        | 61.59        | 51.37        | 88.13        |
| 25           | 346.40       | 404.85       | 228.11       | 150.36       | 110.02       | 112.00       | 65.94        | 55.24        | 93.81        |

### Table 3. The calculated bulk modulus \( B \), shear modulus \( G \), Young’s modulus \( E \), for GdBa\(_2\)Cu\(_3\)O\(_7\)-\(x\). The values were calculated from the constant \( C_{ij} \) [18]. For all the moduli there is an increase in magnitude with the increasing value of pressure up to 20 GPa (optimally doped) then followed by a decrease as the material tends to over doping.

| \( P \) (GPa) | \( B \) (GPa) | \( G \) (GPa) | \( E \) (GPa) |
|--------------|--------------|--------------|--------------|
| 0            | 49.69        | 50.38        | 125.97       |
| 5            | 74.81        | 88.68        | 225.24       |
| 10           | 98.80        | 109.79       | 285.46       |
| 15           | 111.33       | 120.53       | 320.60       |
| 20           | 805.54       | 526.95       | 1412.22      |
| 25           | 108.68       | 115.28       | 310.992      |
The calculated values for the above equations show that the stability criterion is met when the material is subjected to isotropic stress. The Voigt-Reuss-Hill averages were used to convert the anisotropic values of the constant to isotropic.

### 3.3. Debye temperature

Debye temperature is a thermodynamic quantity in material science that is associated with the phonon vibrational modes in a crystal, elastic constant, and specific heat. For isotropic elastic medium it is given by [19]:

\[
\Theta_D = \frac{h}{k} \left( \frac{3n \rho}{4\pi M} \right)^{\frac{1}{3}} v_m
\]

Where \(v_m\) is the average sound velocity, \(h\) is the Planck’s constant, \(N_A\) is the Avogadro’s number, \(k\) is the Boltzmann’s constant, \(\rho\) is the density and \(M\) is the molecular weight of the sold material. The calculated values of the Debye temperature at different pressures have been shown in table 4. The calculated Debye values are used to calculate the superconducting transition temperature using equation (1). The average sound velocity is expressed as,

\[
v_m = \frac{1}{3} \left( \frac{2}{v_l} + 1 \right)^{\frac{1}{3}}
\]

Where \(v_l\) and \(v_t\) are the longitudinal and transverse sound velocities and are calculated from the Bulk modulus \(B\) and the shear modulus \(G\) [20].

### 3.4. Superconductivity transition temperature under pressure

The condition of applying the BCS theory and the Mc Millan equation (equation (1)) in the cuprate superconductor, is that they must undergo doping to populate the holes in the CuO2 layer. For the GdBa2Cu3O7−x [6,7]. This is so since the BCS theory only applies for doped cuprate superconductor and when the superconducting electron flow to the Cu2+ ion, they repel electrons in the O2− ion to the other Cu2+ ion to create a hole (doping). Doping can be achieved in two ways; reducing the concentration of oxygen atoms or inducing pressure to the crystal. When subjected to external pressure, charge concentration near the Fermi level of the crystal lattice increases which modifies the electronic structure. In these groups of materials, superconductivities are a function of polar ionic and doping effects. This effectively promotes the hoping oxygen between the layers and thus influences superconductivity and superconductivity transition temperature. The superconductivity transition temperature resulting from pressure induction doping is represented in table 4. The electron-phonon coupling constant used for the study was \(\lambda = 3.9\) [21].

Induced holes under pressure and the superconductivity transition temperature for the cuprate superconductors are related by the equation of the inverted parabola expressed by the equation [22]:

\[
T_C = T_C(\text{max}) [1 - B(n_op - n)^2]
\]

### Table 4. The calculated Fermi energy (EF), Debye Temperature (\(\Theta_D\)), Average sound velocity (\(v_m\)) and the superconductivity transition temperature (\(T_C\)) for GdBa2Cu3O7−x. The values were calculated from the moduli in table 3. Doping starts at \(T_C = 67.92\) K.

| \(P\) (GPa) | \(EF\) | \(\Theta_D\) (K) | \(v_m\) (M/s) | \(T_C\) (K) |
|---------|--------|----------------|-------------|-------------|
| 0       | 9.55   | 409.00         | 2551.76     | 67.92       |
| 5       | 9.85   | 463.11         | 2939.09     | 77.08       |
| 10      | 10.52  | 495.99         | 3128.50     | 82.20       |
| 15      | 11.09  | 511.42         | 3213.91     | 84.86       |
| 20      | 13.62  | 850.39         | 6375.56     | 141.16      |
| 25      | 11.04  | 465.44         | 3496.60     | 83.59       |
| 30      | 13.10  | 403.35         | 3154.52     | 77.47       |
| 35      | 15.33  | 334.54         | 2451.43     | 60.32       |
| 40      | 18.54  | 225.10         | 1579.71     | 54.33       |
Where $n_{op}$ is the hole concentration in which the $T_C$ attains its maximum value $T_C(\text{max})$ (figure 1). The constant $B = (n_{op} - n_{min})^{-2}$, where $n_{min}$ is the minimum hole concentration when superconductivity starts to appear. Equation (6) can be modified to include pressure and can be presented by [22]:

$$
T_C(P) = T_C(\text{max})(P)[1 - B(n_{op} - n(P))^2]
$$

(7)

Where $T_C(P)$, $T_C(\text{max})(P)$ and $n(P)$ are measured at pressure $(P)$. The model assumes that $n_{op}$ and $B$ are independent of the pressure. By taking $T_C(\text{op})(P)$ to be pressure-dependent $T_C$ at maximum hole concentration then equation (6) can be written as:

$$
T_C(P) = \frac{T_C(\text{op})(P)[1 - B(n_{op} - n(P))^2]}{[1 - B(n_{op} - n_{op}(P))^2]}
$$

(8)

Equation (8) represents the under-doped crystal. As pressure increases, $n(P)$ may approach $n_{op}$ and thus the $T_C$ will be maximum under the conditions of doping by inducing pressure. In this work, it is approximated to happen at around 20 GPa (table 4). The increase of $T_C$ (table 4) as a result of pressure-induced doping up $T_C(\text{max})$ can be attributed to the increase in charge carriers in the CuO$_2$ Planes of GdBa$_2$Cu$_3$O$_{7-x}$ as it happens for all cuprate superconductors [23]. The charge carrier increases the density of state near the Fermi level and thus increases of Fermi energy up to the over doping limit (table 4). The calculated values of $T_C$ show that the material is a good high temperature superconductor and this is supported by the fact that the values for the Debye temperature are also high [24]. Better $T_C$ means the material is stable [25,26] and can be evidenced by the stability criterion (equation (3)).

4. Conclusion

Superconductivity transition temperature has been measured by pressure doping. The use of the Mc Millan’s formula that requires the application of the Debye temperature calculated from the elastic constants. The materials are optimally doped at around 20 GPa. The obtained results confirm the ability of pressure to induce doping and hence enhance superconductivity transition temperature up to optimum doping level. The optimal superconductivity transition temperature is found to be above the normal transition temperature.

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Data availability statement

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

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