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Elastic behavior, pressure-induced doping and superconducting transition temperature of $GdBa_2Cu_3O_{7-x}$

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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 $GdBa_2Cu_3O_{7-x}$ 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 ~20 GPa was the over doping regime where a decrease in T_C was recorded. The highest calculated T_C (max) was ~141.16 K. The results suggest that pressure of ~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 [5]. 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 $GdBa_2Cu_3O_{7-x}$ 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 $GdBa_2Cu_3O_{7-x}$ 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 $GdBa_2Cu_3O_{7-x}$ was $4f^7 5d^1 6s^2$ for Gadolinium, $6s^2$ for Barium, $3d^{10}4s^1$ for Copper and $2s^2 2p^4$, for Oxygen. The convergence threshold used was 10^{-8}eV 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 $6 \times 6 \times 2$. 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]:

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

Where θ_D is the Debye temperature, μ^* is the renormalized Coulomb repulsion and its value is chosen to range from 0.1–0.2 [11,12] and λ is the electron-phonon coupling constant. The application of BCS theory in the calculation of superconducting transition temperature for cuprate superconductors ($GdBa_2Cu_3O_{7-x}$) 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 $GdBa_2CuO_{7-x}$. 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).

Table 1. Calculated lattice parameters (a, b, c in Å) of $GdBa_2Cu_3O_7$ 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
30	3.7952	3.8598	11.2871
35	3.7852	3.8431	11.2458
40	3.7783	3.8263	11.1536

Table 2. Calculated elastic constants C_{ij} (*GPa*) of $GdBa_2Cu_3O_{7-1}$ 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_{44}	C_{55}	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	87.13	312.79	−915.02	4.34	2040.02	2158.10	129.25	−774.49	288.13
25	246.40	304.85	228.11	130.63	89.04	83.61	54.49	42.96	81.38

Table 3. The calculated bulk modulus (***B***), shear modulus (***G***), Young's modulus (***E***), for $GdBa_2Cu_3O_{7-x}$.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	310.092

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] :

$$C_{ijkl} = \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}} \tag{2}$$

Where $\partial \sigma_{ij}$ and ε_{kl} are the applied stress and the Eulerian strain tensors respectively.

The orthorhombic crystal for the $GdBa_2Cu_3O_{7-x}$ 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 $GdBa_2Cu_3O_{7-x}$ under zero pressure and the isotropic condition is satisfied by the following conditions [16,17].

Table 4. The calculated Fermi energy (EF), Debye Temperature (Θ_D), Average sound velocity (V_m) and the superconductivity transition temperature (T_C) for $GdBa_2Cu_3O_{7-x}$.The values were calculated from the moduli in table 3. Doping starts at $T_C = 67.92$ K.

$P(GPa)$	E_F	$\Theta_D(K)$	$v_m(M/s$	$T_c(K)$
0	9.55	409.00	2551.76	67.92
5	9.85	463.11	2939.09	77.08
10	10.52	495.99	3129.50	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

$$C_{ii} > 0(i = 1, 4, 5, 6) > 0,\ (C_{11} + C_{22} - 2C_{12}) > 0,\ (C_{11} + C_{33} - 2C_{13}) > 0,\ (C_{22} + C_{33} - 2C_{23}) > 0,\ (C_{11} + C_{22} + C_{33} + 2C_{12} + 2C_{13} + 2C_{23}) > 0,\ \frac{1}{3}(C_{12} + C_{13} + C_{23}) < B < \frac{1}{3}(C_{11} + C_{22} + C_{33}) \tag{3}$$

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]:

$$\Theta_D = \frac{h}{k}\left[\frac{3n}{4\pi}\frac{N_A\rho}{M}\right]^{\frac{-1}{3}} v_m \tag{4}$$

Where v_m is the average sound velocity, h is the Plank's constant, N_A is the Avogadro's number, k is the Boltzmann's constant, ρ 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,

$$v_m = \frac{1}{3}\left[\frac{2}{v_t^3} + \frac{1}{v_l^3}\right]^{\frac{-1}{3}} \tag{5}$$

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 CuO_2 layer. For the $GdBa_2Cu_3O_{7-1}$ [6,7]. This is so since the BCS theory only applies for doped cuprate superconductor and when the superconducting electron flow to the Cu^{2+} ion, they repel electrons in the O^{2-} ion to the other Cu^{2+} 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]:

$$T_C = T_C(\max)[1 - B(n_{op} - n)^2] \tag{6}$$

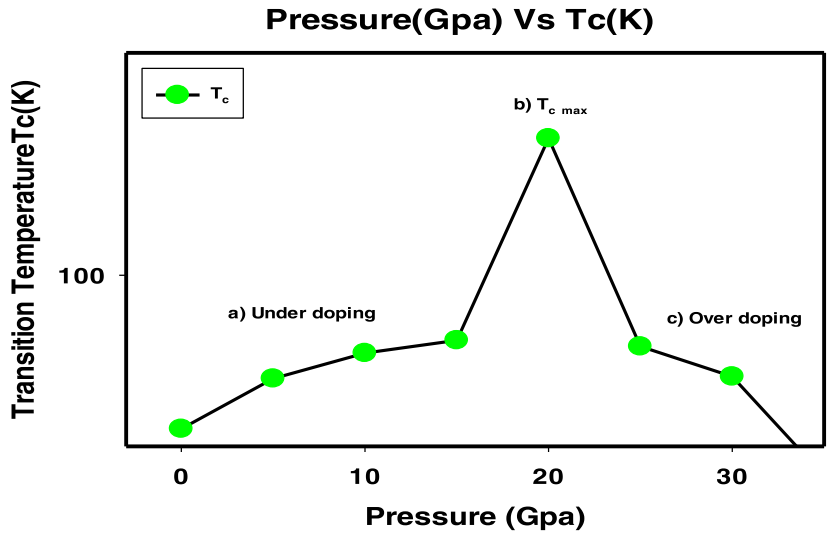

Figure 1. A plot for hole doping for the $GdBa_2Cu_3O_{7-x}$ and different pressure. The T_C starts to rise at $n > n_{\min}$ in the under doping region and achieves a peak at $n = n_{op}$ which represents the T_C (max) for the material under induced pressure doping. At T_C (max) the material is optimally doped. At $n > n_{\max}$ the T_C drops to minimum and the T_C is described by over doping region.

Where n_{op} is the hole concentration in which the T_C attains its maximum value $T_C(\max)$ (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]:

$$T_C(P) = T_C(\max)(P)[1 - B(n_{op} - n(P))^2] \tag{7}$$

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

$$T_C(P) = \frac{T_{C(op)}(P)[1 - B(n_{op} - n(P))^2]}{[1 - B(n_{op} - n_{op}(P))^2]} \tag{8}$$

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 $T_C(\max)$ can be attributed to the increase in charge carriers in the CuO_2 Planes of $GdBa_2Cu_3O_{7-1}$ 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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