



# Predictive physical study of two different crystalline forms of glucose

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## ABSTRACT

The GGA functional PW91 were used in order to predict the structural, electronic, optical and elastic properties of  $\alpha$  and  $\beta$  of D-Glucose. Such compounds, in their solid form, are widely used in chemical and pharmaceutical industry. The pure crystalline forms of glucose  $\alpha$ -D-glucose and  $\beta$ -D-glucose have the same space group (McDonald and Beevers, 1950) [1]. We note that despite the fact that the two compounds have the same space group, upon cooling, the interatomic distances change and a new compound occurs. On the other hand, the cooling also influences the physical properties (structural, elastic, electronic and optical properties). The objective of this paper is associated with the control of the physical states of molecular materials when they are subjected to polymorphic changes. The laws and physical parameters that govern these transformations remain fundamentally misunderstood.

## 1. Introduction

Certain chemical species can give crystals belonging to crystal or different groups depending on the temperature and pressure conditions. These species are said to be polymorphic and correspond to allotropic varieties. Iron is a metal which, depending on the temperature, exhibits an obvious metallic polymorphism. A crystalline solid with a centered cubic (bcc) structure at ambient temperature ( $\alpha$ -iron), a face-centered cubic (fcc) structure obtained from 912 °C ( $\gamma$ -iron), beyond 1394 °C, it becomes a centered cubic (bcc) ( $\delta$ -iron). Another example of polymorphism corresponds to the case of tin, of which we know at least three varieties for the solid form. We'll talk about the two main ones: white tin (ordinary) and gray tin. Although they are made up of identical atoms, the allotropic forms of a chemical compound can often have different physical properties (color, hardness, melting point, electrical conductivity, thermal conductivity) and chemical reactivity.

Carbohydrates are a set of substances whose basic units are simple sugars called oses or monosaccharides. Carbohydrates are an integral part of the structure of many fundamental biological macromolecules, they have the formula  $C_n(H_2O)_n$ .

According to their structures, carbohydrates are subdivided into aldoses and ketoses. Emil Fischer [2] arbitrarily chose the symbol D for the dextrorotatory enantiomer, i.e. the compound which deflects the plane of polarized light to the right (clockwise)

Glucose in two different crystalline forms  $\alpha$  and  $\beta$ -D-Glucose has been studied. We will seek in particular to determine whether or not there is a

coupling between the dynamics of anomeric inter-conversion  $\alpha$ -Glucose $\leftrightarrow\beta$ -Glucose and the slow structural relaxations characteristic of the vitreous state using Density Functional Theory (DFT).

Glucose can exist in three different crystalline varieties:  $\alpha$ -D-glucose (it melts at 158 °C and enthalpy of 198 J/g),  $\beta$ -D-glucose (it melts at 160 °C and enthalpy of 160 J/g) and  $\alpha$ -glucose monohydrate. Modern DFT simulation codes can calculate a vast range of structural, chemical, optical, spectroscopic, elastic, vibrational and thermodynamic phenomena. To understand the crystalline structure of compounds, crystallography is one of the best methods of revealing the structure. The field of crystallography is constantly expanding and evolving, and the introduction of new methods which use the latest technologies makes it possible to elucidate larger and more complex biological systems, which are now becoming useable for structuring the solution. Molecular modeling using Density Functional Theory method DFT were used to calculate the structural, elastic, electronic and optical properties of  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose. Generally, the calculated data indicate that there aren't similarities in bond lengths of these molecules. The results obtained were compared with experimental data. Mc Donald and Beevers [1,3] have fully determined the  $\alpha$ -D-Glucose crystal structure, using Fourier and least-squares methods. In the works of Brown G. M et al. [4], the least squares refinement method did not understand adjustment of extinction parameters, it is for this reason that it was necessary to complete the refinement using the original data, applying the anisotropic extinction corrections [5]. G. M. Brown et al. [6], determined more precisely cell parameters on which our work is based.

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C. Molteni et al. [7] studied the crystalline structures of  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose by means of *ab initio* calculations. For  $\beta$ -D-Glucose compound which for the first time determined by W. G. Ferrier [8], and its structure was refined experimentally, the cell parameters after have been refined by the full-matrix least-squares method [9,10]. The refinement of the crystal structure of  $\beta$ -D-Glucose compound, have been anisotropically from, the results are confirmed by XRD diffraction [11]. The objective of this paper is associated with the control of the physical states of molecular materials when they are subjected to polymorphic changes. The laws and physical parameters that govern these transformations remain fundamentally misunderstood. Furthermore, the DFT (GGA/PW91) was also used. The structure of the two molecules  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose were calculated. The computed GGA/PW91 was compared with those obtained experimentally.

## 2. Computational details

CASTEP code [12] is a software developed at the University of Cambridge UK (Cambridge Sequential Total Energy Package) which uses density functional theory (DFT) to simulate properties, surfaces and interfaces for a wide range of material classes. The density functional calculations on the structural, electronic, and optical properties of  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose were performed using the CASTEP code. Both lattices were optimized to get the equilibrium structure for orthorhombic  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose crystals respectively. The exchange-correlation function was treated by both the generalized gradient approximation (GGA-PW91) [13]. Also, the pseudopotentials constructed using the *ab initio* norm conserving scheme to describe the valence electron interaction with the atomic core, in which the C ( $2p^22s^2$ ), O ( $2p^42s^2$ ) and H( $1s^1$ ) orbitals are treated as valence electrons. The Brillouin zone (BZ) sampling was carried out using the  $2 \times 1 \times 4$  for orthorhombic structures of  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose set of Monkhorst-Pack mesh [14].

The structures were optimized, using the Broyden-Fletcher-Goldfarb-Shenno (BFGS) minimization technique, in order to archiving the most stable structure in their local area. Self-consistent convergence condition setting: the total energy was less than  $0.2 \cdot 10^{-4}$  eV/atom, the force in each atom was less than  $0.05$  eV/Å, the offset tolerance was less than  $0.002$  Å and the Stress bias was less than  $0.1$  GPa.

## 3. Structural properties

The structural parameters  $a$ ,  $b$  and  $c$  and the atomic positions of  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose are reported in Tables 1 and 3, and show a good agreement with previous experimental values [6,11]. The electronic band diagram was built along the lines of high symmetry on the principal directions of BZ in reciprocal space (it's the same either for  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose), which connect the following high symmetry points (in the terms of the reciprocal lattice unit vectors):  $\Gamma(0; 0; 0)$ ;  $Z(0; 0; 0.5)$ ;  $T(-0.5; 0; 0.5)$ ;  $Y(-0.5; 0; 0)$ ;  $S(-0.5; 0.5; 0)$ ;  $X(0; 0.5; 0)$ ;  $U(0; 0.5; 0.5)$ ;  $R(-0.5; 0.5; 0.5)$  are shown in Fig. 1. An orthorhombic lattice was found for  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose by Brown et al. [6] and Shirley et al. [11] with space group  $P2_12_12_1$ , respectively.

The lattice parameters of  $\alpha$ -D-Glucose ( $a = 10.366$ ,  $b = 14.850$ ,  $c = 4.975$ ),  $\beta$ -D-Glucose ( $a = 9.205$ ,  $b = 12.640$ ,  $c = 6.654$ ) with four formula units per unit cell. The gray, red and white balls represent C, O and H atoms respectively as shown in Fig. 2.

The relative deviation % of the optimized volume and cell parameters computed at 0 K, with respect to the experimental ones, are reported in Table 3.

More precisely, our computed lattice constants show respectively an error of 2.3%, 0.42% and 6.11% [3.53%, 0.87%, and 2.62%]. This relative deviation is due to the fact that our calculation corresponds to the perfect bulk material at zero temperature, whereas the experimental one was synthesized at high temperature. Our calculated ratio  $c/a$  and  $c/b$  (0.497, 0.354) [0.716, 0.535] for ( $\alpha$ -D-Glucose) [ $\beta$ -D-Glucose], are in

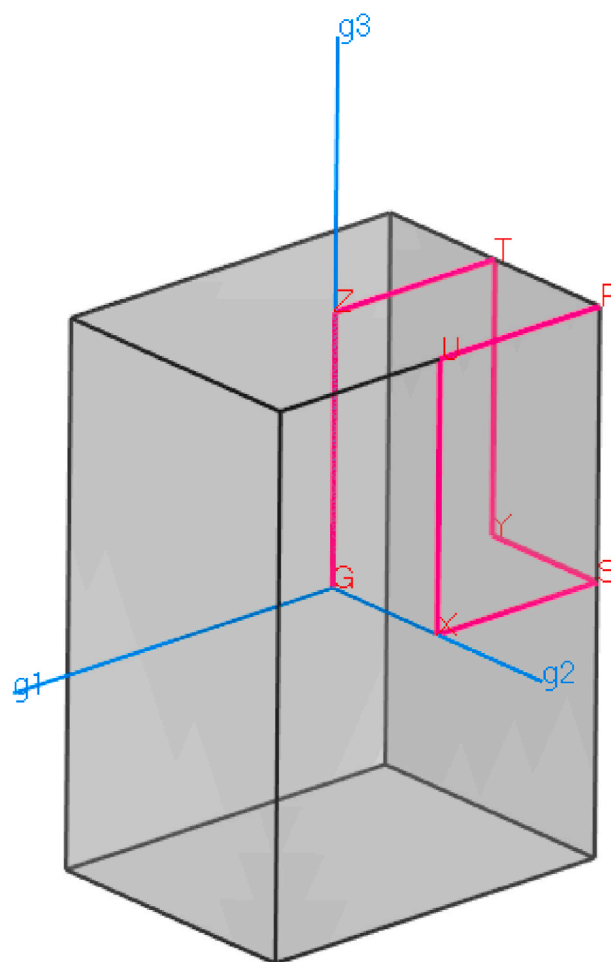


Fig. 1. The Brillouin zone (BZ) of a unit cell for the  $\alpha$ -D-Glucose.

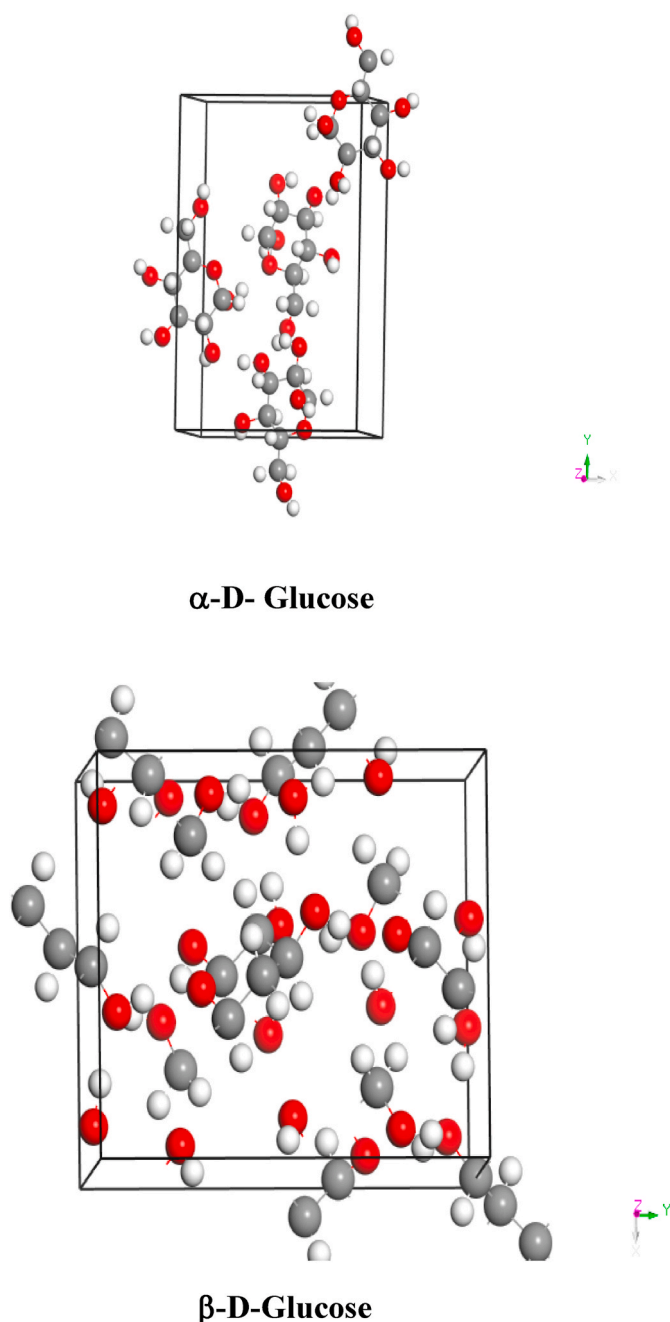
reasonable accord with the experimental considered data (0.479, 0.335) [0.722, 0.526]. The results are listed in Table 3. The Calculated atomic coordinates are compared with experimental ones (in parentheses) of  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose. The results of structural parameters of the two crystalline phases are listed in Tables 1 and 2. Tables 1–3, contain a summary of the experimental and optimized structural data for  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose. Comparison of the calculated and experimental results yields good agreement between them, which makes a firm basis for reliability of the subsequent analysis of the electronic, elastic and optical properties of these materials. A qualitative comparison of the transition enthalpy  $E$  between the two phases showed that the  $\alpha$ -phase is more stable than the  $\beta$  one of 39 meV at 0 K.

## 4. Elastic constants

Subject to low stress, a crystal deforms linearly with respect to this constraint. When the stress is removed, the material returns to its standard state so it is reversible. This behavior observed for all materials is said to be elastic. By imposing a chosen deformation, we can determine the elastic constants of the material. The energy of system under constraint is expressed as follows [15]:

$$E(V, \delta) = E(V_0, 0) + V_0 \left[ \sum_i \tau_i \xi_i \delta_i + \frac{1}{2} \sum_{ij} C_{ij} \delta_i \xi_i \delta_j \right] \quad (1)$$

where  $E(V_0, 0)$  is the energy of the unstrained system with equilibrium volume  $V_0$ ,  $\tau_i$  is an element in the stress tensor, and  $\xi_i$  is a factor to take care of Voigt index.



**Fig. 2.** Representation of the orthorhombic structure of  $\alpha$ -D- Glucose and  $\beta$ -D-Glucose which has four molecules per unit cell (the carbon atoms are gray, the oxygen atoms are in red while those of hydrogen are in white color). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

The elastic constants  $C_{ij}$  of solids describe the link between mechanical and dynamical behaviors. It is well known that the first-order and second-order derivatives of the potential give forces and elastic constants, respectively. These, moreover, are increased as the system symmetry is reduced. In the cases therefore studied, with orthorhombic structure, there are a total of nine independent elastic constants  $C_{11}$ ,  $C_{22}$ ,  $C_{33}$ ,  $C_{44}$ ,  $C_{55}$ ,  $C_{66}$ ,  $C_{12}$ ,  $C_{13}$  and  $C_{23}$ .

The elastic constants of  $\alpha$ -D-Glucose and  $\beta$ -D-glucose at zero pressure are found to satisfy the stability criteria for orthorhombic crystal [16]:

$$C_{ii} > 0 \ (i = 1, 2 \dots 6), \ C_{11} + C_{22} - 2C_{12} > 0, \ C_{11} + C_{33} - 2C_{13} > 0, \ C_{22} + C_{33} - 2C_{23} > 0 \text{ and } (C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})) > 0. \quad (2)$$

**Table 1**

Calculated BFGS atomic coordinates and compared with experimental ones (in parentheses) of  $\alpha$ -D Glucose[5].

Element	x	y	z
H	0.3928(0.3957)	0.6780(0.6776)	0.2354(0.2599)
H	0.5624(0.5675)	0.5566(0.5565)	0.3227(0.3385)
H	0.6182(0.6171)	0.3818(0.3792)	0.1139(0.1034)
H	0.4794(0.4805)	0.3919(0.3945)	0.2986(0.3114)
H	0.7177(0.7246)	0.7155(0.7136)	0.1277(0.1178)
H	0.7448(0.7517)	0.5093(0.5081)	0.2368(0.2323)
H	0.4253(0.4127)	0.2801(0.2860)	0.0777(0.0700)
H	0.4415(0.4486)	0.7728(0.7776)	-0.2206(-0.2032)
H	0.2763(0.2752)	0.5633(0.5674)	-0.4124(-0.4299)
H	0.5117(0.5134)	0.4843(0.4865)	-0.2144(-0.2310)
H	0.5909(0.5888)	0.6552(0.6541)	-0.1809(-0.1994)
H	0.2362(0.2326)	0.6090(0.6123)	-0.0251(-0.0155)
C	0.3352(0.3329)	0.5979(0.6007)	-0.0792(-0.0761)
C	0.4177(0.4184)	0.6737(0.6745)	0.0332(0.0453)
C	0.5589(0.5610)	0.6516(0.6514)	0.0178(0.0152)
C	0.5822(0.5859)	0.5560(0.5568)	0.1172(0.1200)
C	0.5161(0.5141)	0.3938(0.3953)	0.1038(0.1025)
C	0.4949(0.4955)	0.4862(0.4886)	-0.0084(-0.0121)
O	0.7128(0.7175)	0.5336(0.5348)	0.0762(0.0687)
O	0.6264(0.6334)	0.7153(0.7153)	0.1679(0.1632)
O	0.3660(0.3654)	0.5130(0.5153)	0.0364(0.0369)
O	0.4577(0.4458)	0.3248(0.3311)	-0.0449(-0.0517)
O	0.3848(0.3879)	0.7578(0.7598)	-0.0771(-0.0655)
O	0.3491(0.3471)	0.5957(0.6006)	-0.3419(-0.3540)

**Table 2**

Calculated BFGS atomic coordinates and compared with experimental ones (in parentheses) of  $\beta$ -D-Glucose [10].

Element	x	y	z
H	0.0072(0.0100)	0.2541(0.2520)	0.6899(0.6760)
H	0.2636(0.2710)	0.1937(0.1960)	-0.1048(-0.1090)
H	0.2698(0.2890)	0.2932(0.2920)	0.0774(0.0710)
H	0.2264(0.2380)	0.1252(0.1250)	0.2260(0.2180)
H	0.1151(0.1160)	0.1315(0.1370)	0.5275(0.5400)
H	0.0987(0.0850)	0.3712(0.3700)	-0.0719(-0.1200)
H	-0.2032(-0.2120)	0.0280 (0.0200)	0.6069(0.6220)
H	-0.0471(-0.0410)	0.1173(0.1070)	-0.0097(-0.0080)
H	0.0726(0.0810)	-0.0397(-0.0350)	0.2833(0.2960)
H	-0.1756(-0.5134)	0.1088(0.1040)	0.3367(0.3370)
H	0.0533(0.0670)	-0.0020(-0.0020)	-0.1789(-0.1960)
H	-0.0908(-0.0850)	-0.1352(-0.1280)	-0.1615(-0.1880)
C	0.0183(0.0198)	0.1630(0.1614)	0.4592(0.4610)
C	-0.0778(-0.0786)	0.0729(0.0717)	0.3926(0.3902)
C	-0.0148(-0.0081)	0.0074(0.0059)	0.2261(0.2259)
C	0.0420(0.0486)	0.0784(0.0764)	0.0621 (0.0600)
C	0.1379(0.1479)	0.1636(0.1614)	0.1496(0.1486)
C	0.1999(0.2099)	0.2389(0.2385)	-0.0005(-0.0027)
O	-0.0553(-0.0611)	0.2279(0.2279)	0.5845(0.5825)
O	-0.1087(-0.1119)	0.0073(0.0060)	0.5590(0.5587)
O	-0.1206(-0.1147)	-0.0615(-0.0647)	0.1482(0.1445)
O	0.1198(0.1297)	0.0191(0.0173)	-0.0784(-0.0825)
O	0.0581(0.0636)	0.2242(0.2220)	0.2891(0.2893)
O	0.0942(0.0992)	0.2958(0.2936)	-0.1059(-0.1079)

The elastic constants  $C_{11}$ ,  $C_{22}$ ,  $C_{33}$  are obtained by inducing uniaxial deformations to the crystalline axes  $a$ ,  $b$ ,  $c$ , respectively.

The elastic shear constants  $C_{44}$ ,  $C_{55}$  and  $C_{66}$  provide information on the binding properties between adjacent planes of atoms. They are therefore useful for determining the stability of the crystal structure. We are left with three more elastic constants  $C_{12}$ ,  $C_{13}$ , and  $C_{23}$ . Unlike the stability criteria, we used the opposite sign of the elastic constants of  $\alpha$ -D Glucose ( $\beta$ -D-glucose)  $C_{12}$ ,  $C_{13}$  ( $C_{13}$ ) compounds and this is necessary to complete this study. The sign of  $C_{12}$  and  $C_{13}$  does not affect the value of one of the global properties of  $\alpha$ -D-Glucose and  $\beta$ -D-glucose. The orthorhombic  $\alpha$ -D-Glucose and  $\beta$ -D-glucose has three lattice parameters  $a$ ,  $b$  and  $c$ , with Bravais lattice vectors  $(a, 0, 0)$ ,  $(0, b, 0)$  and  $(0, 0, c)$ . This structure is shown in (Fig. 2). The stress tensor components are related

**Table 3**

The unit cell dimensions a, b, c and cell volume V obtained experimentally [5, 10] in parenthesis and by using geometry optimization for  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose.

	$\alpha$ -D Glucose	$\beta$ -D-Glucose
Function	GGA(PW91)	GGA(PW91)
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> )	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> )
Lattice parameter:a(Å)	10.611(10.366)	9.530(9.205)
b(Å)	14.913(14.850)	12.750(12.640)
c(Å)	5.279(4.975)	6.829(6.654)
c/a	0.497(0.479)	0.716(0.722)
c/b	0.354(0.335)	0.535(0.526)
Cell volume (Å <sup>3</sup> )	835.536	829.883
Z	4	4
Calculated density (g cm <sup>-3</sup> )	1.4322	1.4419 (1.545)
	1.560 [2]	
Number of atoms in cell	24	24
Energy (eV)	-14842.478	-14842.339

to the strain tensor elements through the generalized Hooke's law (elastic deformation is a linear function of stresses (stress-strain)), which can be expressed as [17].

$$\sigma_{ij} = C_{ijkl}\epsilon_{kl} \Rightarrow \sigma_i = C_{ij}\epsilon_j \quad (3)$$

in which  $\sigma_i$  is a stress tensor element  $i = 1-6$ .  $\epsilon_j$  is a strain tensor element  $j = 1, 6$ .  $C_{ij}$  is an elastic constant matrix element  $i = 1, 6; j = 1, 6$ . The stiffness's matrix of an orthorhombic system is given by nine [18]. The elastic constants of the orthorhombic structure of  $\alpha$ -D-Glucose and  $\beta$ -D-glucose at zero pressure and 0 K are presented in Table 4.

## 5. Anisotropy

The mechanical properties of the materials depend on their regular microstructural properties. It is well known that microcracks are induced in materials owing to the anisotropy of the coefficient of thermal expansion as well as elastic anisotropy [19]. Hence to understand these properties it is important to calculate elastic anisotropy. The anisotropic behavior has an important implication in engineering science as which well as in crystal physics. What interests us in our study is the shear anisotropic factors provide a measure of the degree of anisotropy in the bonding between atoms in different planes.

For  $\alpha$ -Glucose and  $\beta$ -Glucose with orthorhombic structure the shear anisotropic factor for the {100} shear planes between the <011> and <010> directions are

$$A_1 = \frac{4C_{44}}{C_{11} + C_{33} - 2C_{13}} \quad (4)$$

For the {010} shear planes between <101> and <001> directions it is

$$A_2 = \frac{4C_{55}}{C_{22} + C_{33} - 2C_{23}} \quad (5)$$

and for the {001} shear planes between <110> and <010> directions it is

$$A_3 = \frac{4C_{66}}{C_{11} + C_{22} - 2C_{12}} \quad (6)$$

The shear anisotropic factors obtained from our theoretical values are given in Table 5. For an isotropic crystal the factors  $A_1$ ,  $A_2$ , and  $A_3$

**Table 4**

Calculated at zero pressure the elastic moduli ( $C_{ij}$ ),  $B_V$  and  $G_V$  of orthorhombic of  $\alpha$ -D-Glucose and  $\beta$ -D-glucose.

	$C_{11}$	$C_{22}$	$C_{33}$	$C_{44}$	$C_{55}$	$C_{66}$	$C_{12}$	$C_{13}$	$C_{23}$	$B_V$	$G_V$
$\alpha$ -D Glucose	40	36	1	1	10	1	-2	-4	2	7	7
$\beta$ -D-Glucose	13	112	18	22	15	20	28	-2	33	29	17

**Table 5**

Zero temperature shear anisotropy factors  $A_i$  ( $i = 1,2,3$ ), and B/G ratio all dimensionless of  $\alpha$ -Glucose and  $\beta$ -Glucose obtained from first-principles calculations are shown.

	$A_1$	$A_2$	$A_3$	B/G
$\alpha$ -Glucose	0.082	1.025	0.05	1
$\beta$ -Glucose	1.257	0.937	1.159	1.70

must be one. It is a measure of the degree of elastic anisotropy possessed by the crystal if any value smaller or greater than unity. S.F. Pugh [20] proposed the B/G ratio to represent a measure of a "machinable behavior". A high B/G value is then associated with ductility and a low value with brittleness. The critical value which separates ductile and brittle behaviors is at about 1.75. For instance, diamond has a B/G of 0.80 [21]. The results of our calculations give B/G of 1 [1.70] for  $\alpha$ -D-Glucose [ $\beta$ -D-glucose], which should behave like brittle materials, our compounds B/G ratio are reported in Table 5. The variation in volume, density, crystal structure, elastic constants ( $C_{12}$ ,  $C_{13}$ ) in  $\alpha$ -D-Glucose and ( $C_{13}$ ) in  $\alpha$ -Glucose and  $\beta$ -Glucose, reveals that there is a structural relaxation characteristic of the anionic conversion  $\alpha$ -Glucose  $\rightarrow$   $\beta$ -Glucose, the slow structural relaxations characteristic of the state glassy (mechanical properties (anisotropy) are improved)).

## 6. Electronic structure

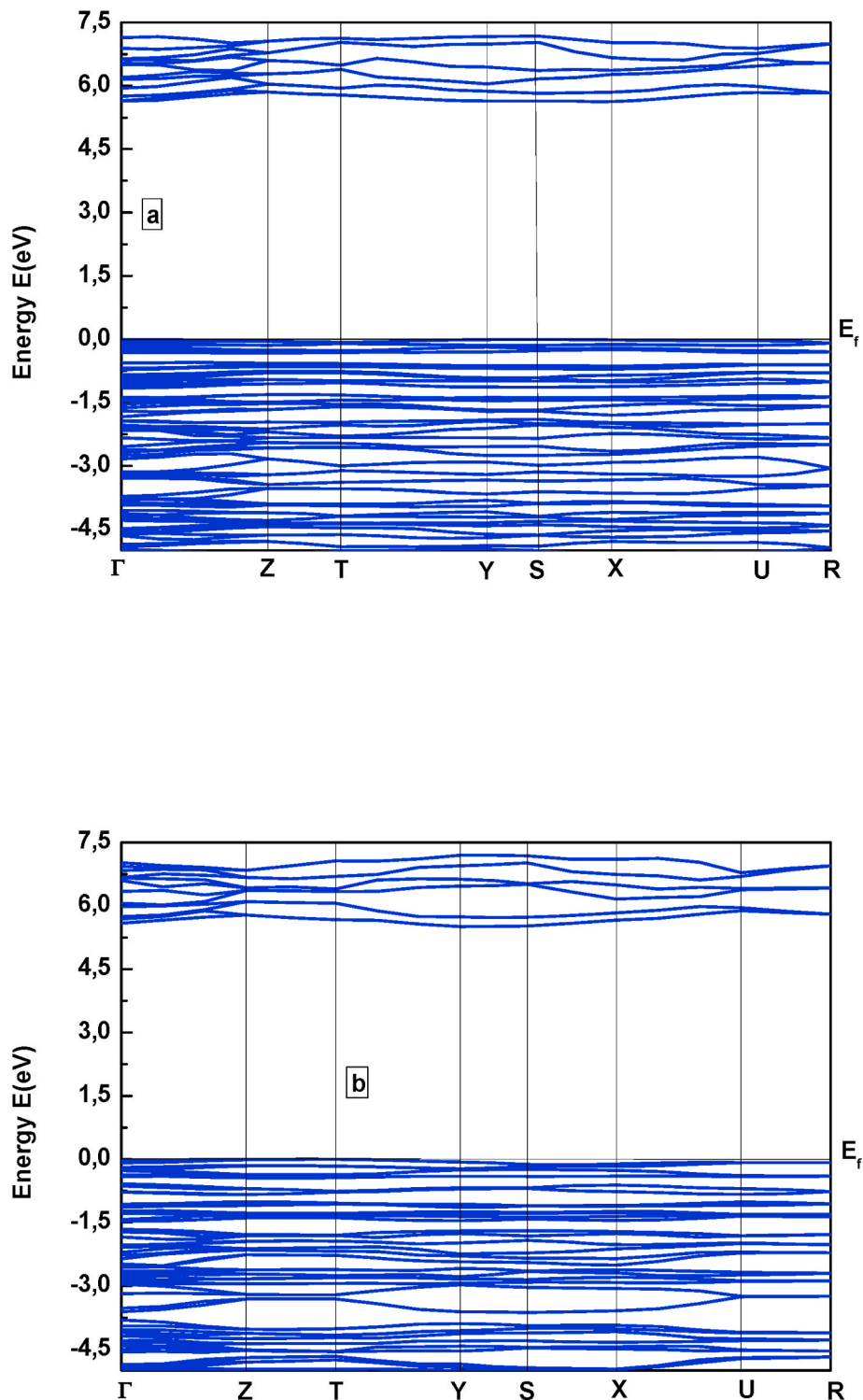
Fig. 3 presents both calculated band structures of  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose. The band gap is of a direct nature for  $\alpha$ -D-Glucose, since the maximum of the valence band and the minimum of the conduction band are both situated at the BZ center, similarly to the case of  $\beta$ -D-Glucose. The partial *s*- and *p*- Densities of States (DOS) for all compounds in orthorhombic structure at equilibrium lattice constants.  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose structures have similar DOS profiles in the whole energy region except of some differences. One can notice that the conduction band is of about 8 eV. It is made basically of the C 2*p* states with admixture with the H 1*s* states (Fig. 4). For  $\alpha$ -D-Glucose, the C-(*s*, *p*) and O-*s* states lie near -20 eV with small amounts of the H 1*s* states. The bands in the energy range between -15eV and 0 eV are constituted of C-*s* mixed with C-*p* dominated by bands O-*p* and a small contribution of H-*s*.  $\beta$ -D-Glucose show similar structure as that of  $\alpha$ -D-Glucose, in the exception where the electronic contribution to the  $\alpha$ -D-Glucose structure is ahead of that of  $\beta$ -D-Glucose and this is due to the difference in interatomic and intermolecular distances.

## 7. Optical properties

When a rectilinearly polarized light interacts with a molecule, the electronic cloud of the molecule depends on the ability of the electrons to polarize (polarization noted  $\alpha$ ), i.e. the electronic cloud to acquire a dipole moment  $\vec{P}$  under the effect of an electric field  $\vec{E}$ . The cloud is multidimensional, so the polarization can be represented by a tensor (link between the field  $\vec{E}$  and the polarization  $\vec{P}$ ). The knowledge of both real and imaginary parts of the complex dielectric function  $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$  allows calculation of important optical functions. The real part  $\epsilon_1(\omega)$  of the dielectric function  $\epsilon(\omega)$  which is obtained by a Kramers-Kronig analysis.

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \quad (7)$$

The imaginary part  $\epsilon_2(\omega)$  is calculated from the momentum matrix



**Fig. 3.** Electronic band structure of the orthorhombic ( $\alpha$ ,  $\beta$ )-D-Glucose along high symmetry directions in the Brillouin zone (BZ): (a)  $\alpha$ -D-Glucose, and (b) the  $\beta$ -D-Glucose.

elements between occupied and unoccupied wave functions within selection rules. The real part  $\epsilon_1(\omega)$  of dielectric function  $\epsilon(\omega)$  follows from Kramers-Kronig relations.

$$\epsilon_1(\omega) - 1 = \frac{2}{\pi} P \int_0^{\infty} \frac{\omega' \epsilon_2(\omega')}{\omega'^2 - \omega^2} d\omega' \quad (8)$$

$$\epsilon_2(\omega) = -\frac{2\omega}{\pi} P \int_0^{\infty} \frac{\epsilon_1(\omega') - 1}{\omega'^2 - \omega^2} d\omega' \quad (9)$$

where P implies the principal value of the integral.

In this section, we discuss the optical properties of the orthorhombic ( $\alpha, \beta$ )-D-Glucose compounds. The linear response of the system to an external electromagnetic field with a small wave vector is measured

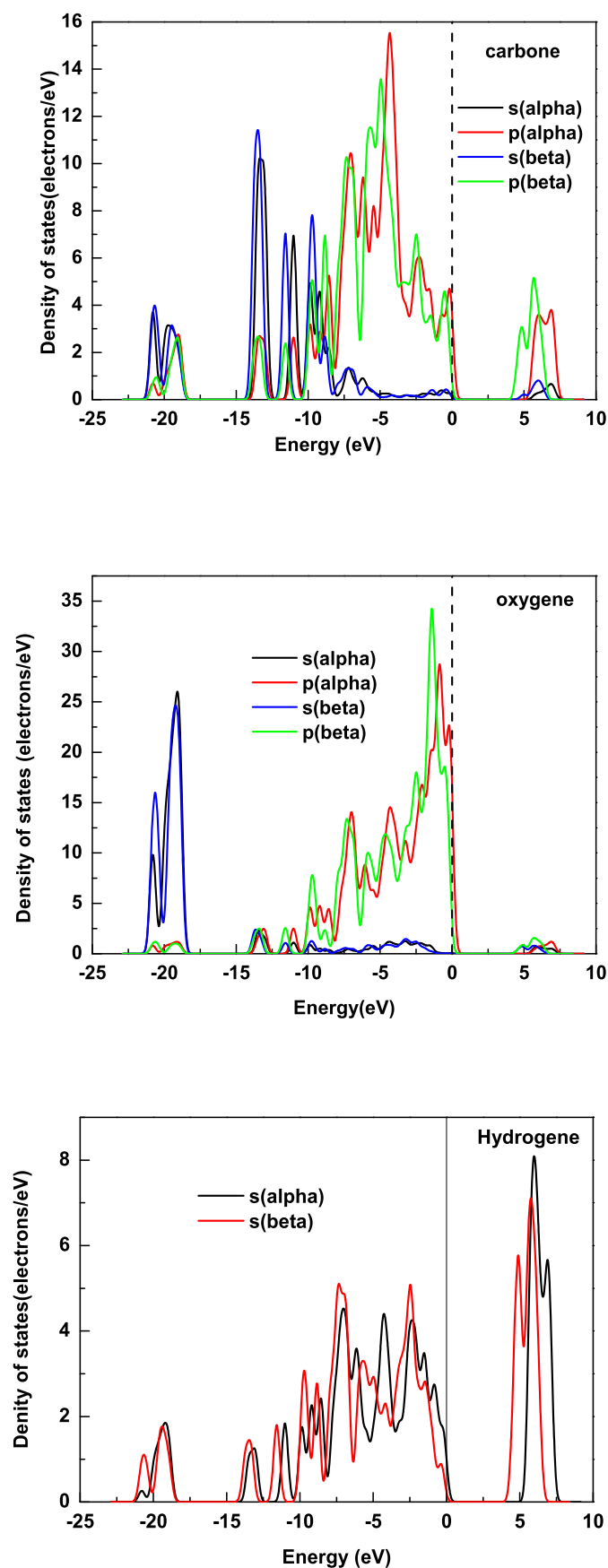


Fig. 4. Partial density of states (PDOS) per atoms of the orthorhombic  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose along high symmetry directions in the Brillouin zone (BZ).

through the complex dielectric function. The absorption edges spectrum of ( $\alpha$ ,  $\beta$ )-D-Glucose crystal are almost similar and appear at about 70 nm. The absorption spectra showed a considerable shift towards ultraviolet for  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose, with absorption maxima at 113.44 nm, 107.20 nm and calculated band gap energy of 5.63 eV, 5.50 eV respectively. Fig. 5 shows the calculated spectra reflectivity (a), absorption function (b) and loss function of the orthorhombic ( $\alpha$ ,  $\beta$ )-D-Glucose crystal. They have a narrow peak of the orthorhombic  $\alpha$ -D-Glucose [ $\beta$ -D-Glucose], it is the same remark of the calculated dielectric function, refractive index and optical conductivity, (Fig. 6).

Reflectivity spectra show almost non-selective behavior over a wide wavelength range in the ultraviolet region.  $\alpha$ -D-glucose and  $\beta$ -D-glucose are efficient absorbers of ultraviolet radiation, their refractive indices are very high in the ultraviolet to visible range. All this is due to the difference in interatomic and intermolecular distances.

## 8. Population analysis

Atomic populations Analysis (Mulliken populations Analysis) of ( $\alpha$  and  $\beta$ )-D-Glucose compounds allows to describe qualitatively the evolution of charge transfers and binding interactions in a series of homologous molecular systems as  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose compounds. It highlights certain aspects of atomic interactions. For  $\beta$ -D-glucose the absolute Mulliken charge values of nearest neighbors for hydrogen (0.24–0.52), carbone (0.22–0.23) and oxygen (−0.76 to −0.52) and average distances (H–C = 1.02872 Å to 1.10829 Å); (H–O = 0.97260 Å to 0.99369 Å) and (C–O = 1.38238 Å to 1.45000 Å), see Tables 6 and 7.

Experimental results [22] indicate that the melting temperature of crystalline  $\alpha$ -D-glucose (146 °C) precedes that of  $\beta$ -D-glucose (150 °C). We notice that the mean interatomic distances are in total agreement with those given experimentally either in  $\alpha$ -D-glucose or  $\beta$ -D-glucose, which means that the DFT is a good calculation tool for this type of compounds. There are no experimental values of the bands for comparison especially for H–H bonds. We can observe that they show the same trend, but with larger deviations. The comparison is made over the distances C–C, C–O for  $\beta$ -D-glucose rather than H–C and H–O. The GGA (PW91) results are in good agreement with experimental data for  $\alpha$ -D-glucose and  $\beta$ -D-glucose.

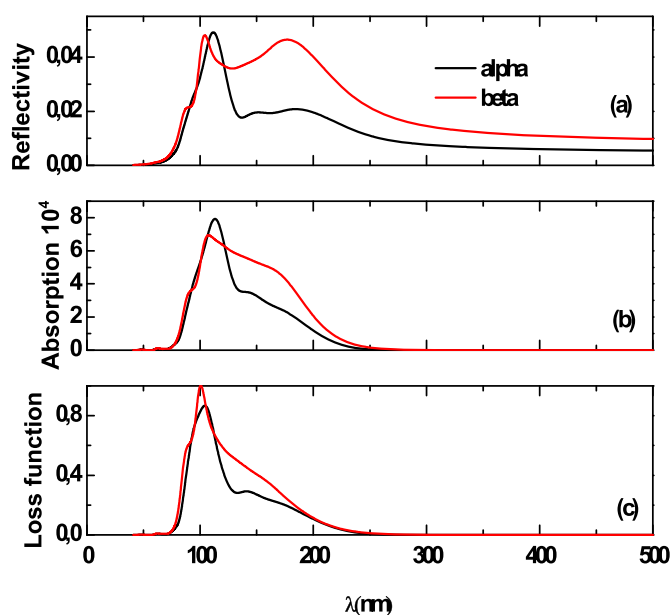
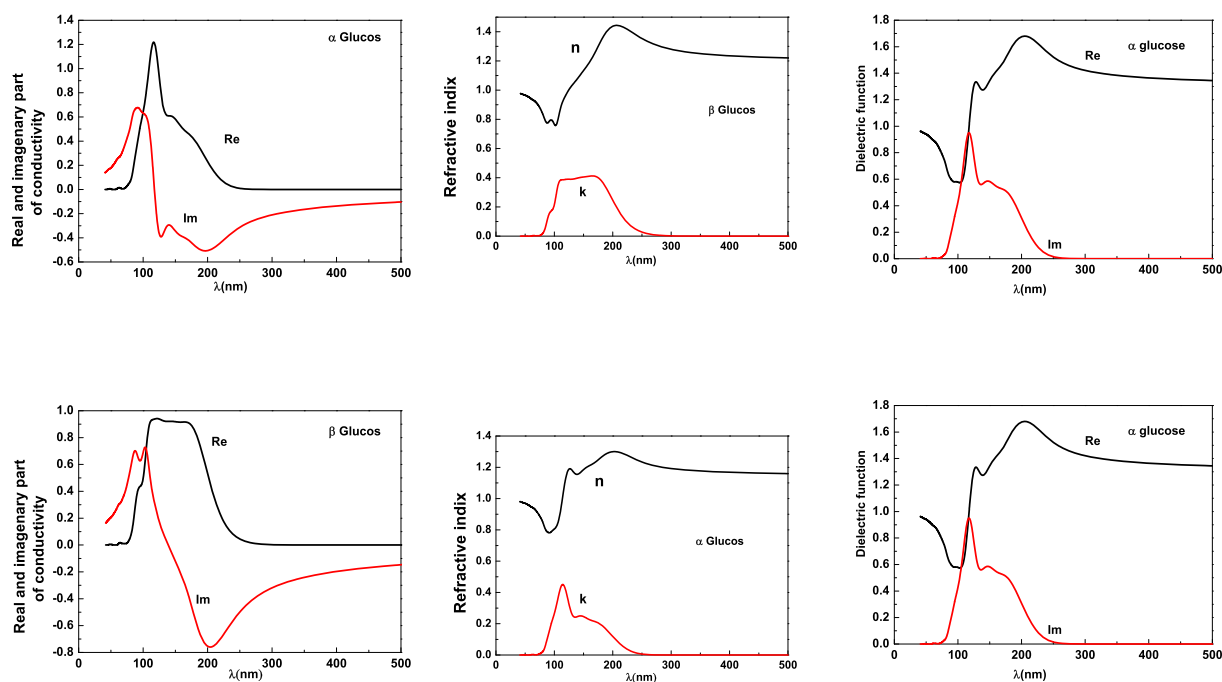


Fig. 5. The calculated (a) reflectivity, (b) absorption function and (c) loss function of the orthorhombic  $\alpha$ -D-Glucose and  $\beta$ -D-Glucose crystal.



**Fig. 6.** Real (solid black line) and imaginary (solid red line) components of the calculated dielectric function, refractive index and optical conductivity of the orthorhombic ( $\alpha$ ,  $\beta$ )-D-Glucose crystal. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

**Table 6**

Atomic populations (Mulliken) of all electron configurations of atoms for  $\alpha$ -D-glucose and  $\beta$ -D-glucose.

Species	s-Orbitals	p-Orbitals	Total	Charge (e)
<u><math>\alpha</math>-D-glucose.</u>				
H	0.49–0.75	0.00	0.49–0.75	0.25 to 0.51
C	1.12–1.23	2.68–3.00	3.80–4.23	0.20 to –0.23
O	1.78–1.81	4.75–4.96	6.53–6.77	–0.75 to –0.53
<u><math>\beta</math>-D-glucose.</u>				
H	0.48–0.72	0.00	0.48–0.72	0.24 to –0.52
C	1.11–1.23	2.67–3.01	3.78–4.24	0.22 to –0.23
O	1.78–1.82	4.74–4.96	6.52–6.75	–0.76 to –0.52

**Table 7**

Lengths and overlap populations of the shortest atomic bonds in ( $\alpha$ ,  $\beta$ )-D-Glucose compounds [5,10].

Bond	Population	Length (Å)
<u><math>\alpha</math>-D-glucose</u>		
H–O	–0.13 to 0.54	0.98263 to 0.99253
H–C	–0.19 to 0.87	1.09908 to 1.10492 (1.112–1.127)
C–O	–0.17 to 0.58	1.39531 to 1.4444 (1.400–1.431)
C–C	–0.19 to 0.74	1.51699 to 1.54747 (1.517–1.539)
H–H	–0.12 to 0.03	1.77
<u><math>\beta</math>-D-glucose</u>		
H–O	0.52 to 0.54	0.97260 to 0.99367
H–C	0.83 to 0.87	1.09872 to 1.10829
C–O	0.48 to 0.61	1.38238 to 1.45000 (1.383–1.437)
C–C	0.70 to 0.74	1.52356 to 1.54017 (1.511–1.529)
H–H	–0.10 to –0.01	1.78

## 9. Conclusion

It is with great pleasure that your search leads to previously unknown results. The results presented in this article were very interesting and show promising results after structural, elastic, electronic and optical properties of  $\alpha$ -D-glucose and  $\beta$ -D-glucose in their solid state. The estimated lattice constant is in excellent agreement with the available

experimental values. It is for the first time, the elastic constants were studied and concluded that shear constants  $C_{44}$ ,  $C_{55}$  and  $C_{66}$  provide information on the binding properties between adjacent planes of atoms of  $\alpha$ -D-glucose and  $\beta$ -D-glucose and therefore useful for determining the stability of the crystal structure.

Unfortunately, for the other computed properties in this work, there are no previous calculations and not experimental values for comparison, so some comparisons can only be made with each other. A qualitative comparison of the transition enthalpy  $E$  between the two phases showed that the  $\alpha$ -phase is more stable than the  $\beta$ -phase one of 39 meV at 0 K. The difference in interatomic and intermolecular distances influences the spectra of the calculated optical function.

## Statement of novelty

The statement of Novelty of this paper is associated with the control of the physical states of molecular materials when they are subjected to polymorphic changes. The laws and physical parameters that govern these transformations remain fundamentally misunderstood.

## Declaration of competing interest

The authors whose names are listed immediately below certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; ember ship, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

## References

- [1] T.R.R. McDonald, C.A. Beevers, The crystal structure of  $\alpha$ -D-glucose, *Acta Crystallogr.* 3 (1950) 394.
- [2] M.A. Rosanoff, *J. Am. Chem. Soc.* 28 (1) (1906) 114–121.
- [3] T.R.R. McDonald, C.A. Beevers, *Acta Crystallogr.* 5 (1952) 654–659.

- [4] G.M. Brown, H.A. Levy,  $\alpha$ -D-Glucose:  $\alpha$ -D-glucose: precise determination of crystal and molecular structure by neutron-diffraction analysis, *Science* 147 (1965) 1038–1039.
- [5] P. Coppens, W.C. Hamilton, *Acta Crystallogr. A* 26 (1970) 71–83.
- [6] G.M. Brown, H.A. Levy,  $\alpha$ -D-Glucose:  $\alpha$ -D-glucose: further refinement based on neutron-diffraction data, *Acta Crystallogr. B* 35 (1979) 656–659.
- [7] C. Molteni, M. Parrinello, *Cem. Phys. Lett.* 275 (1997) 409–413.
- [8] W.G. Ferrier, *Acta Crystallogr.* 16 (1963) 1023.
- [9] R. Shiono, Oak Ridge Least Squares Program Modified for the, Crystallograph Laboratory of the University of Pittsburgh, 1966.
- [10] W.R. Busing, K.O. Martin, H.A. Levy, Fortran Crystallographic Least Squares Program. ORNL-TM-305, Oak ridge National Laboratory, Tennessee, 1962.
- [11] Shirley S.C. Chu, G.A. Jeffrey, *Acta Crystallogr. B* 24 (1968) 830.
- [12] M.D. Segall, P.J.D. Lindan, M.J. Probert, C.J. pickard, P.J. Haspin, S.J. Clark, M. C. Payne, *J. Phys. Condens. Matter* 14 (2002) 2717.
- [13] J.P. Perdew, S. Burke, M. Ernzerhof, *Phys. Rev. Lett.* 78 (E) (1997) 1396.
- [14] H.J. Monkhorst, J.D. Pack, *Phys. Rev. B* 13 (1976) 5188.
- [15] L. Fast, J.M. Wills, B. Johansson, O. Eriksson, *Phys. Rev. B* 51 (1995) 17431.
- [16] C. Jiang, *Scripta Mater.* (2010) 532.
- [17] J.F. Nye, *Physical Properties of Crystals*, Oxford University Press, Ely House, London, 1957.
- [18] M.J.P. Musgrave, *Crystal Acoustics: Introduction to the Study of Elastic Waves and Vibrations in Crystals*, Holden-Day, San Francisco, CA, 1970.
- [19] V. Tvergaard, J.W. Hutchinson, *J. Am. Chem. Soc.* 71 (~1988) 157.
- [20] S.F. Pugh, *Philos. Mag. A* 45 (1954) 823.
- [21] J. Haines, J.M. leger, G. Bocquillon, *Synthesis and design of superhard materials*, *Annu. Rev. Mater. Res.* 31 (2001) 1–23.
- [22] D.R. Lide, *Handbook of Chemistry and Physics*, CRC, Baco Raton, Etats-Unis, 1993-1994.