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Elastic properties, Debye temperature, density of states and electron–phonon coupling of ZrB_{12} under pressure

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ABSTRACT

The structural parameters, elastic constants and the electronic density of states of ZrB_{12} under pressure are determined using first-principles calculations with plane-wave pseudopotential density functional theory, within the generalized gradient approximation. From the elastic constants the elastic parameters and Debye temperature were calculated. They increase as the pressure is increased. The density of states at the Fermi level decreases as pressure is increased, changing from 0.576 to 0.515. Using the Debye temperature and the McMillan equation, the electron–phonon coupling constant was obtained as a function of pressure. It is found that the electron–phonon coupling constant is proportional to the logarithm of the ratio between the value of the Debye temperature and the value of the superconducting critical temperature.

1. Introduction

The discovery of superconductivity in MgB_2 with superconducting critical temperature (T_c) of about 40 K [1] has generated a great deal of interest, and many studies related to fundamental and practical aspects of this material have been performed. This discovery motivated the reinvestigation of compounds containing boron, for example, MB_2, MB_4, MB_6, MB_{12} and MB_{66}, with M a transition metal or rare-earth element. Between the dodecaborides, ZrB_{12} has the highest superconducting critical temperature ($T_c \approx 6$ K) [2–4]. In order to understand its superconducting behavior, this compound has been studied widely [3–14]. In particular, a negative pressure effect on T_c was observed from magnetization measurements under pressure [5]. Band structure calculations suggest that superconductivity can be caused by Zr 4d electrons contribution to the electronic density of states at the Fermi level [15].

Elastic properties of solids are closely related to many fundamental solid-state properties, such as the equation of state, specific heat, thermal expansion, Debye temperature (θ_D), Gruneisen parameter, melting point, and many others. From the elastic constants, one can obtain valuable information about the binding characteristics between adjacent atomic planes, the anisotropic character of the bonding, and the structural stability. In addition, the behavior of materials under pressure, based on calculations or measurements, has become quite interesting in the recent years as it provides insight into the nature of the solid-state properties and determines values of fundamental parameters.

The elastic constants and the electronic density of states (DOS) under pressure (P) are among the characteristics of ZrB_{12} which are not yet calculated, also the effect of pressure over the electron–phonon coupling constant (λ_{ep}). In this work, we performed *ab initio* calculations of the elastic constants and the DOS of ZrB_{12} under pressure. The mechanical properties and θ_D were determined from the elastic constants. The electron–phonon coupling constant as a function of pressure was calculated using the McMillan equation, taking as parameters θ_D, the Coulomb pseudopotential (μ^*) and T_c. The value of μ^* was determined from the electronic density of states at the Fermi energy ($N(E_F)$).

2. Method of calculation

The lattice parameter, elastic constants and the electronic density of states of ZrB_{12}, at different pressures, were calculated with the Cambridge Serial Total Energy Package software (CASTEP), with the plane wave pseudopotential code [17,18]. The exchange–correlation energy functional was treated with the generalized gradient approximation with Perdew and Wang parametrization (GGA-PW91) [19]. The energy cut-off for the plane-wave basis was of 360 eV. The sampling of the Brillouin zone was of $9\times9\times8$ k-points with a Monkhorst–Pack grid [20]. The convergence tolerances were: total energy of 10^{-6} eV/atom, the maximum force on atoms of 0.002 eV/Å, maximum atomic displacement of 10^{-4} Å, and the maximum strain amplitude of 0.003. The structure of ZrB_{12} is cubic with a space group $O_h^5 - Fm3m$ (No. 225) [2]. The Wyckoff position of Zr is 4*a* (0, 0, 0) and for boron is 48*i* (1/2, 0.166, 0.166). The Zr atoms and cuboctahedral B_{12} clusters are arranged in an NaCl like structure. The 52 atoms fcc unit cell of ZrB_{12}

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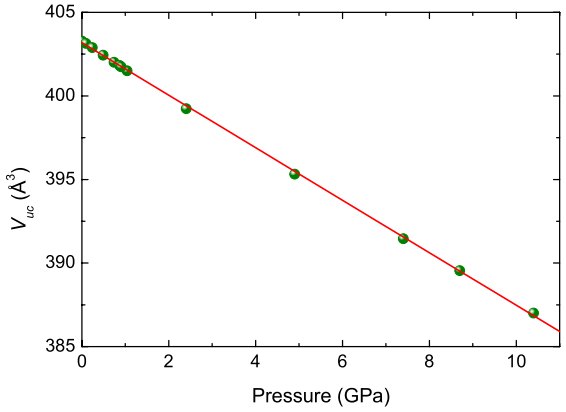

Fig. 1. Unit cell-volume V_{uc} as a function of pressure of ZrB_{12}. The continuous line is a linear fit of the calculated values.

is characterized by single lattice parameter. The symmetry of the cubic structure of ZrB_{12} reduces the elastic constants to: C_{11}, C_{12} and C_{44}. The elastic properties were calculated in a polycrystalline ceramic material, treated as an aggregate of single crystals at random orientation, using the Voigt and Reuss approximation [21,22].

The Debye temperature was calculated by the following equation [23],

$$\theta_D = \frac{\hbar}{k_B}\left[\frac{6\pi^2 N}{V}\right]^{1/3} v_m,$$

where $\hbar$ is Plank's constant, k_B is Boltzmann's constant, N is the number of atoms in the unit cell, v_m is the average sound velocity. v_m depends on v_l and v_t, the longitudinal and transverse elastic wave velocities, respectively, which are obtained from Navier's equations [24].

The electron–phonon coupling constant can be determined using the semiempirical formula of McMillan [25], expressed as:

$$\lambda_{ep} = \frac{1.04 + \mu^* \ln(\theta_D/1.45T_c)}{(1 - 0.62\mu^*)\ln(\theta_D/1.45T_c) - 1.04}.$$

In this equation, μ^* is the Coulomb pseudopotential that is related to the screened Coulomb interaction. μ^* is determined using the empirical relation [26]

$$\mu* = 0.26\frac{N(E_F)}{1 + N(E_F)}$$

where $N(E_F)$ is the electronic density of states at the Fermi energy obtained from first-principles calculations.

3. Results and discussion

Table 1 shows the optimized lattice parameter a, the unit cell-volume (V_{uc}) and the elastic parameters of ZrB_{12} obtained from the calculations as a function of the pressure. The value of the lattice parameter obtained at zero pressure (7.3882 Å) is in good agreement with previous reports [2,16,27]. With the increase of pressure the lattice parameter and the unit cell volume decreases. The volume changes about 4% in the calculated pressure range. This percentage is similar to the change of volume observed in Cu and $La_{1.85}Sr_{0.15}CuO_4$ under similar pressure [28]. Fig. 1 shows $V_{uc}(P)$ calculated values, the trend of this data is linear. In this figure, the continuous line is a linear fit of the data that gives the equation of state $V_{uc}(P) = 403.18 - 1.57P$.

The elastic constant values obtained fulfill the mechanical stability conditions of a cubic structure, these are: $C_{11} + 2C_{12} > 0$, $C_{11} - C_{12} > 0$ and $C_{44} > 0$. The values showed in Table 1 for zero pressure are consistent with the experimental and theoretical

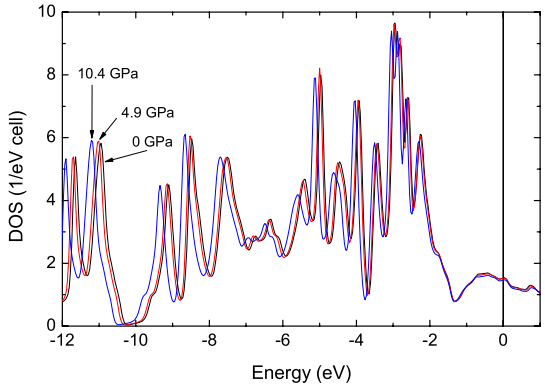

Fig. 2. Total electronic density of states, DOS, of ZrB_{12} at different pressures.

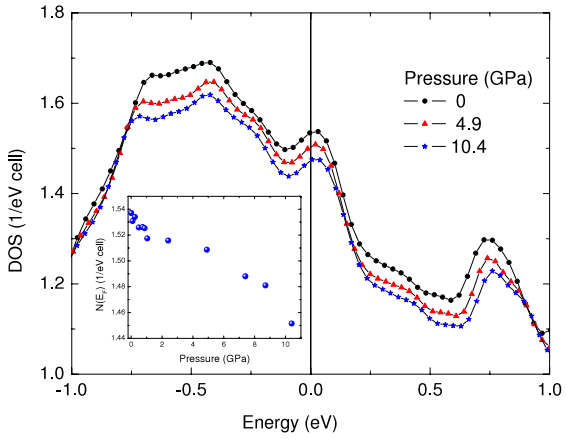

Fig. 3. Total electronic density of states of ZrB_{12} under pressure around the Fermi energy. The inset shows $N(E_F)$ against pressure.

values reported [16]. As expected, the elastic constants increase as the pressure increases, also the bulk modulus (K), the shear modulus (G) and Young's modulus (E). The ratio K/G increases with the pressure of about 7% in the calculated pressure range. The behavior of mechanical parameters as a function of pressure indicates that ZrB_{12} is more isotropic and becomes hard with the increment of pressure.

The Poisson ratio obtained for ZrB_{12} is between 0.10 and 0.12. These values indicate that bonding in ZrB_{12} is covalent. However, the bonding between Zr and B atoms is of ionic character, whereas a complicated mixture of covalent bond and a small contribution of metallic bond are present in the B–B bonds [16]. Covalent materials typically has $\nu = 0.1$ and for metallic materials is between 0.25 to 0.35 [29].

The total density of states of ZrB_{12} at different pressures are shown in Fig. 2. This figure depicts curves for 0, 4.9 and 10.4 GPa. The DOS at zero pressure is similar to the reported calculations [10]. The main electronic contribution to the DOS in ZrB_{12} is due to 2p orbital of B and 4d orbital of Zr, with $N(E_F) = 1.687$ 1/eV cell [10,15]. As can be seen in Fig. 2, the effect of pressure on the orbital contributions to the DOS is small in the range of the considered pressures. However, changes on $N(E_F)$ are observed. Fig. 3 displays the pressure dependence of the total density of states of ZrB_{12} near the Fermi energy (zero energy corresponds to the Fermi energy (E_F)). The calculated equilibrium density of states at E_F, at zero pressure, is 1.576 1/eV cell, which is in agreement with the reported value [15]. The increment of pressure produces a decrement in $N(E_F)$, inset of Fig. 3. The decrement of $N(E_F)$ between zero pressure and $P = 10.4$ GPa is just about 5.6%.

Table 1
Lattice parameter (a), unit-cell volume V_{uc}, elastic constants (C_{ij}), bulk modulus (K), shear modulus (G), Young's modulus (E), Poisson's ratio (ν) and percentage of shear (A_G) of polycrystalline ZrB_{12} calculated with the Voigt and Reuss assumptions at different pressures (P).

P (GPa)	a (Å)	V_{uc} (Å^3)	C_{11}	C_{44}	C_{12}	K (GPa)	G (GPa)	K/G	E (GPa)	ν	A_G
0.0	7.3882	403.29	414.2	243.7	139.8	231.3	255.5	0.91	560.2	0.10	0.17
0.09	7.3873	403.14	414.0	243.9	139.4	231.0	255.7	0.91	560.4	0.10	0.17
0.24	7.3858	402.90	414.7	244.2	140.3	231.8	255.9	0.91	561.1	0.10	0.16
0.49	7.3830	402.44	415.5	244.3	140.2	232.0	256.2	0.91	561.9	0.10	0.17
0.74	7.3805	402.02	416.8	244.8	140.5	232.6	256.9	0.91	563.3	0.10	0.18
0.87	7.3792	401.82	417.1	244.7	141.1	233.1	256.7	0.91	563.4	0.10	0.17
1.04	7.3773	401.51	418.5	245.0	141.1	233.6	257.5	0.91	565.0	0.10	0.19
2.4	7.3634	399.24	426.8	248.5	146.8	240.1	260.6	0.92	574.1	0.10	0.17
4.9	7.3393	395.32	448.6	253.5	164.7	259.4	265.2	0.98	593.4	0.12	0.15
7.4	7.3152	391.46	448.8	257.4	161.7	257.4	268.9	0.96	598.3	0.11	0.14
8.7	7.3033	389.55	454.9	259.9	166.0	262.3	271.1	0.97	604.9	0.12	0.13
10.4	7.2878	387.01	463.1	262.4	170.7	268.2	274.0	0.98	613.2	0.12	0.14
Exp. [16]	443	265	129	234	–	–	–	–	–		
Calc. [16]	–	–	–	249	–	–	–	–	–		

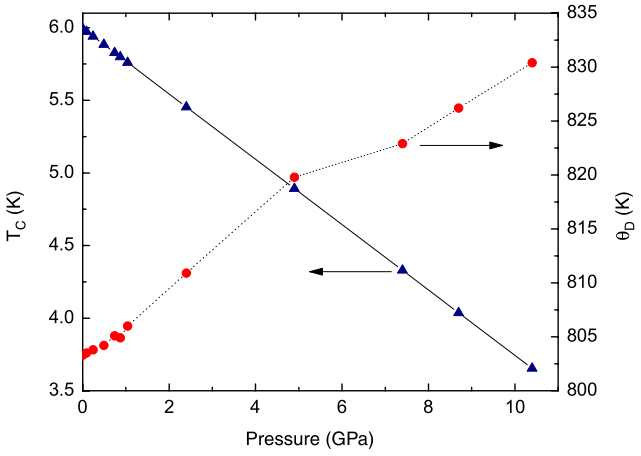

Fig. 4. Superconducting critical temperature T_c and Debye temperature θ_D as a function of pressure. The T_c values at pressures below 1.04 GPa are experimental values [5].

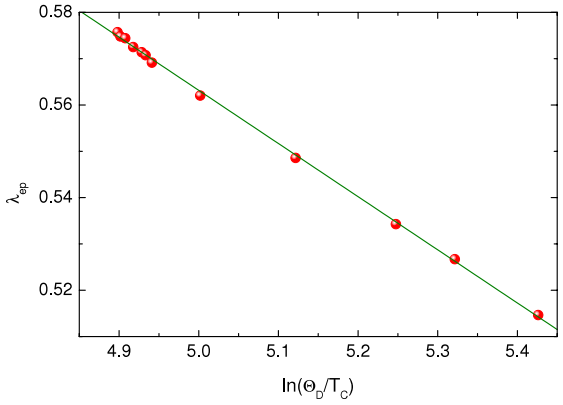

Fig. 5. Electron–phonon coupling constant λ_{ep} against the logarithm of the ratio of Debye temperature θ_D and superconducting critical temperature T_c related by pressure.

The Debye temperature calculated from the elastic constants and the superconducting transition temperature, at different pressures, are shown in Fig. 4. The T_c values for pressure $\leq$1.04 GPa are experimental values [5] and for pressures $>$1.04 GPa. T_c was obtained from a linear extrapolation of the experimental data. Therefore, T_C decreases as the pressure increases. θ_D increases from 803 to 830 K with pressure. Debye temperature obtained from specific heat measurements on ZrB_{12} is between 1000 and 1260 K [4,16]. These values depend on the temperature range where they were determined. These values are higher than θ_D obtained from our calculations; however, it is expected because calculations were done at $T = 0$ K. Note that θ_D obtained in this work is of the same order as that of θ_D (830 K) reported for MgB_2 [30]. The fact that θ_D increases with pressure seems to indicate that T_c must increase; however there are other variables that modify the superconducting transition temperature. It is noteworthy that T_c can be modified by the electron–phonon coupling and the electronic density of states at the Fermi level, characteristics that are modified by pressure. The decrement of T_c is according to the decrease in $N(E_F)$ as the BCS theory predicts [31]. This behavior is alike to that observed in MgB_2 [32].

The electron–phonon coupling constant was calculated by the McMillan equation [25]. In the range of pressure studied, calculations indicate that λ_{ep} decreases from 0.576 to 0.515. For zero pressure, the electron–phonon coupling values reported are: 0.58 [13,33] and 0.68 [6]. These values and our results indicate that the electron–phonon coupling in ZrB_{12} is weak. $\lambda_{ep} \approx 1$ [34] has been reported for MgB_2, determined from theoretical calculations. This λ_{ep} value indicates that MgB_2 is a moderately strong-coupled superconductor. In Fig. 5, we plot λ_{ep} against $\ln(\theta_D/T_c)$. As can be observed the relationship is linear, note that λ_{ep}, θ_D and T_c are correlated by pressure. In this figure, the continuous line is a fitting of the data that gives $\lambda_{ep} = 1.14 - 0.11 \ln(\theta_D/T_c)$; this relationship appears to be proposed by the BCS theory [28]. The fact that λ_{ep} decreases and θ_D increases with pressure indicates that T_c is affected predominantly by $N(E_F)$.

4. Conclusions

In summary, we performed calculations of elastic properties and the electronic density of states of ZrB_{12} under pressure, using plane wave pseudopotential density functional theory, within the generalized gradient approximation. The bulk and shear moduli increases with the pressure, indicating that directional bonding and more symmetric structure is promoted by the pressure. It is found that the elastic constants and the Debye temperature increase monotonically with pressure. Moreover, using θ_D, μ^* and T_c as parameters, the electron–phonon coupling constant was calculated employing the McMillan equation. In the pressure range studied, we found that the electron–phonon coupling constant of ZrB_{12} decreases with pressure and corresponds to a weak-coupled superconductor. Furthermore, λ_{ep} is proportional to $\ln(\theta_D/T_c)$, correlated by pressure. Finally, the density of states of ZrB_{12} at the Fermi level under pressure decreases, which may be responsible for the reduction of the superconducting transition temperature.

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