Computer simulation of phases consisting of Be, B and Li atoms and calculating their elastic properties using quantum mechanical calculation

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Abstract. Chemical elements of groups 1 and 2 have the most pronounced properties in their periods. There is something unique about each of them, inciting substantial interest, especially regarding light-weight alloys of these elements. Young's modulus to density ratio of beryllium is six times higher than that of steel. Heat-resistance of Be is 600°C. The combination of these physicochemical properties makes beryllium alloys specifically applicable in aerospace. Simulation of material properties is one of the main missions for materials science. Elastic properties are the easiest to calculate compared to other mechanical properties. Elastic properties are characterized by the fifth-fourth digits of the total cluster energy. Here we present the results of the calculation of the elastic constants of hexagonal and cubic beryllium and cubic lithium boride. The calculations were based on the density functional theory (DFT). The results obtained by different techniques (quantum chemical, semi-empirical) and data from the literature were compared.

1. Introduction
The CP2K software package was used in this work. It is a freeware distributed under GPL license, has a good syntax description, and supports parallel computing using MPI technology. CP2K is in Fortran 2003.

The strain energy is related to the total crystal energy by the expression:

\[ dE = TdS + V_0 \sum_{ij} \sum_{kl} C_{ijkl}u_{kl}du_{ij} \] (1)

where:
- \( V_0 \) is the initial volume,
- \( dE \) is the change in internal energy,
- \( u \) is the strain tensor,
- \( TdS \) is the heat supplied to the system; \( T, dS \) are the temperature and entropy change, respectively.

To leave out the change in entropy during deformation of the system, all calculations will be carried out at \( T = 0^\circ K \).
After replacing indexes and integration [1], it takes the form:

\[ E = \frac{1}{2} V_0 \sum_i \sum_j C_{ij} u_j u_i \]  

(2)

The minimum number of elastic constants depends on symmetry. In general, the minimum set decreases with increasing symmetry.

The deformation of the crystal must be small for it to remain elastic.

2. Implementation of computing experiments

A special application was written to generate clusters. It sends impurity atoms to positions in the model volume. The operation of this application is based on maintaining the maximum bulk density of impurity atoms.

The existing computer does not allow for ab-inito computations for a cluster of more than 50 atoms because there is not enough RAM. Calculation of the cluster of a Be-Li-B substitutional alloy with such a small number of atoms is a priori incorrect since a random substitution in a small cluster will not be uniform.

2.1. Algorithm for calculating elastic moduli

(1) A cluster is created with “zero” approximation based on data from the literature, ICSD database data or general considerations.

(2) The geometry is optimized by CP2K software within the system of a cluster suspended in the model volume at zero temperature.

(3) The finding of the minimum potential energy is verified by calculating clusters with periods shifted by a small amount. If step (3) = yes, then go to step (4); If step (3) = no, then the minimum search is performed.

(4) Its energy in the undeformed state is calculated under the conditions similar to step (2).

(5) The equation (2) is solved; the strain tensor is found to calculate the elastic constants of interest.

(6) The cluster is calculated in the state deformed according to the strain tensor under the conditions similar to step (4).

(7) The elastic parameters are calculated from the energy difference using the equation from step (6).

2.2. Cubic beryllium, \( \beta \)-Be

\( \beta \)-Be has a BCC lattice with a period of 2.249 Å and is stable at temperatures above 1250°C. It is, perhaps, more flexible than \( \alpha \)-Be[2]. The results (Table 1) for the elastic moduli \( C_{11} \) and \( C_{12} \) showed a large scatter of values between the values obtained with the relative compression of \( u = 0.1 \) and with \( u = 0.07 \) and \( u = 0.05 \). We also noticed that this phase “was eager” to move from the cubic to the hexagonal crystal system, which is quite consistent with the fact that it is a high-temperature modification.

This modification is metallic, like the low-temperature one, since the distribution of the electron density level with an electron concentration of \( 3 \cdot 10^{24} \text{ cm}^{-3} \) (Fig. 1) binds all atoms.

2.3. Cubic lithium boride, BLi

Cubic lithium boride has periods of 4.74 Å. It has a space group Fd\( \overline{3} \)mZ.

No information on the elastic properties of this compound has been found in open sources. Information from paid sources was not used.

Calculated values are presented in the (Table 2).
Table 1. Elastic constants for $\beta$-Be

| $N$, atoms | 36 | 36 | 36 |
|------------|----|----|----|
| $u$ | 0.10 | 0.07 | 0.05 |
| $V_0$, Å³ | 248.83 | 248.83 | 248.83 |
| $E_0$ eV/atom | -399.530 | -399.530 | -399.530 |
| $\Delta E_{c_1+c_{c12}}$, meV/atom | -143 | -41 | -19 |
| $\Delta E_{c_{11}−c_{c12}}$, meV/atom | 7 | 6 | 4 |
| $\Delta E_{c_{55}}$, meV/atom | -86 | -44 | -19 |
| $C_{11}$, GPa | 102 | 158 | 82 | 66 |
| $C_{12}$, GPa | 131 | 174 | 110 | 107 |
| $C_{55}$, GPa | 98 | 100 | 103 | 90 |
| $a$, Å | 2.55$^*$ | | 2.4 |

Table 2. Elastic constants for cubic lithium boride

| $N$, atoms | 16 | 16 | 16 |
|------------|----|----|----|
| $u$ | 0.10 | 0.07 | 0.05 |
| $V_0$, Å³ | 110.59 | 110.59 | 110.59 |
| $E_0$ eV/atom | -139.062 | -139.062 | -139.062 |
| $\Delta E_{c_1+c_{c12}}$, meV/atom | -70 | -34 | -17 |
| $\Delta E_{c_{11}−c_{c12}}$, meV/atom | -39 | -19 | -10 |
| $\Delta E_{c_{55}}$, meV/atom | -56 | -27 | -14 |
| $C_{11}$, GPa | 125 | 126 | 125 | 124 |
| $C_{12}$, GPa | 36 | 36 | 37 | 35 |
| $C_{55}$, GPa | 65 | 65 | 65 | 64 |
| $a$, Å | 4.74$^*$ | | 4.8 |

2.4. Comparison of the results obtained by semi-empirical and quantum mechanical calculations

The semi-empirical potential coefficients were selected on the basis of data on the structure and elastic properties of beryllium, lithium, and boron. Cross coefficients were selected from similar
information on boron diberyllide and lithium boride. The GULP software package was used for the calculations.

A comparison of the calculations showed (Table 3) that the semi-empirical model worked well, even better than quantum mechanical methods, for those substances whose properties were used to select the potential coefficients. Quantum chemical methods always delivered a good result. However, the less similar the substance was to those for which semi-empirical potentials were optimized, the greater was the mismatch between the data obtained by different methods.

Table 3. Comparison of the elastic constants calculated by semi-empirical (SE) and quantum mechanical (QM) methods, as well as experimentally obtained values [\*]; MP marks the data calculated within the “Materials project” database of structural information and phase properties. Like in this paper, the calculations employed the density functional theory.

| Material | a, Å | b, Å | c, Å | C_{11}, GPa | C_{12}, GPa | C_{13}, GPa | C_{33}, GPa | C_{66}, GPa |
|----------|------|------|------|------------|------------|------------|------------|------------|
| Be       | 3.583 | 3.583 | 292  | 27         | 14         | 336        | 163        |
| SE       | 2.262 | 2.262 | 286  | 27         | -7         | 332        | 133        |
| QM       | 2.163 | 3.483 | 295  | 10         | 29         | 194        | 165        |
| MP       | -     | -     | 322  | 21         | 8          | 162        | 151        |
| β-Be     | 2.55  | -     | -    | -          | -          | -          | -          |
| SE       | 2.5   | -     | 250  | 46         | -          | -          | 194        |
| QM       | 2.4   | -     | 102  | 131        | -          | -          | 98         |
| MP       | 2.55  | -     | 153  | 109        | -          | -          | 188        |
| Be_{2}B  | 2.87  | -     | -    | -          | -          | -          | -          |
| SE       | 4.57  | -     | 272  | 68         | -          | -          | 144        |
| QM       | 4.39  | -     | 230  | 67         | -          | -          | 66         |
| MP       | -     | -     | 234  | 108        | -          | -          | 123        |
| BLi      | 4.57  | -     | -    | -          | -          | -          | -          |
| SE       | 6.37  | -     | 83   | 51         | -          | -          | 10         |
| QM       | 4.74  | -     | 125  | 36         | -          | -          | 64         |

3. Conclusions
A technique was developed for first-principle computational experiments to calculate elastic material constants using the CP2K software package. A distinctive feature of this technique is its applicability in the study of metal systems with a complex electron structure caused by electron sharing.

This technique is based on the use of the quantum mechanical method of calculations, wherefore it can be applied to describe the elastic properties of nanoscale structures.

The calculations yield the results close to the experimental values obtained for macrodimensional polycrystalline samples. In this study, elastic constants were calculated for beryllium, boron diberyllide, and lithium boride. Unfortunately, the limited computational resources have precluded the originally conceived calculation of solid solutions for the substitution of the Be-B-Li system. The greatest mismatch between the calculated values of the elastic constants and data from the literature is observed for parameters with small values. The reason is that in their case the loss of information due to the accumulated error is the most pronounced, associated with the limited dimension of mantissa of the numbers.

We carried out a comparative analysis of the results of calculating elastic constants for the phases consisting of beryllium, boron and lithium atoms by semi-empirical and quantum mechanical methods. Semi-empirical methods performed well in describing the substances for
which the potential coefficients were optimized, even better than quantum mechanical methods. Their transferability, however, is rather poor. Quantum chemical methods yield a satisfactory result, but require greater computational resources.

References
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