

# FIRST-PRINCIPLES THERMOELASTICITY OF BERYLLIUM

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# FIRST-PRINCIPLES THERMOELASTICITY OF BERYLLIUM

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**Abstract.** The temperature dependence  $\alpha$  of the shear modulus in beryllium is calculated using two different methods within the framework of Density Functional Theory. In Density Function Perturbation Theory, the usual technique to determine the values of elastic constants at  $T = 0$  K is to access the temperature-dependence of the elastic constants through phonon calculations. The elastic constants are then combined to give the Voigt-Reuss-Hill shear modulus for each phase (hcp and bcc). In Quantum Molecular Dynamics, through a certainly crude assumption, we connect the ratio of mean square displacements at around melting temperature to the temperature-dependence of the shear modulus. With both techniques, we obtain  $\alpha = 0.24 \pm 0.14$ , in good agreement with the model of D.L. Preston and D.C. Wallace [Solid State Comm; 81 277 (1992)].

**Keywords:** modulus, phase diagram, beryllium, ab initio.

**PACS:** 62.20de, 64.70kd, 71.15.Nc, 71.15.Pd .

## INTRODUCTION

The equation of state (EOS) and the constitutive law form the basis for a model of response of a crystal to dynamic loading. In the last few years we [1-3] among other researchers [4-7] have paid much attention to beryllium, especially its phase diagram and elastic constants.

We will focus here on the behavior of the shear modulus  $G$  which is an ingredient of constitutive models such as PTW [8]. It is generally assumed in these models that density and temperature dependencies can be decoupled. The dimensionless measure  $\alpha$  of the temperature dependence of  $G$ , is given by:

$$\alpha = -\frac{T_m(\rho)}{G_0(\rho)} \left( \frac{\partial G}{\partial T} \right)_\rho \quad (1)$$

Here  $T_m$  denotes the melt curve,  $\rho$  the density and  $G_0$  the shear modulus at  $T = 0$ K. For most metals,

$\alpha$  is around  $0.23 \pm 0.08$  [9] and without dedicated experimental data, beryllium is assumed to follow this behavior.

Based on phonon spectrum calculations, we give our *ab initio* prediction of the phase diagram. Then we discuss the behavior of the shear modulus  $G$  for each existing phase.

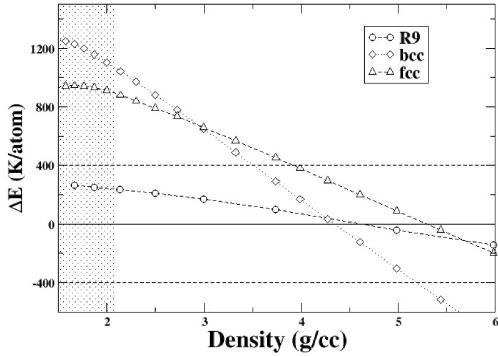
The Density Function Perturbation Theory (DFPT) calculations are performed with the Abinit package [10] using the Goedecker-Teter-Hutter [11] pseudopotential and the Generalized Gradient Approximation (GGA) [12]. Quantum Molecular Dynamics (QMD) calculations [3] are done with the Vienna Ab-initio Simulation Package [18].

## PHASE DIAGRAM

The experimental phase diagram of beryllium is still largely unknown. Few works involving temperature have been published since François and Contre [13]. The experimental evidence of the

hcp-bcc transition under pressure is still missing and depends on the evolution of DAC design. In such situations, *ab initio* calculations are widely used to predict phase diagrams. The Helmholtz free energy of each crystal phase is the sum of  $\phi_0$ , the static lattice potential,  $F_l$ , the quasi-harmonic ion-vibration free energy, and  $F_E$ , the electronic contribution which is included through a Sommerfeld approach.

We compare the stability of four different structures pertinent to beryllium: hcp, bcc, fcc and R9 ( $\alpha$ -Sm type), which is known to appear in martensitic transformation. Figure 1 shows the static lattice potential of the relaxed structures. The hcp structure gets the lowest energy up to 4.5 g/cc. Beyond this density, the bcc phase becomes the more stable phase. At densities lower than 2.1 g/cc the bcc phase is unstable (shaded region in Fig. 1).



**Figure 1.** Cold curves relative to hcp phase for R9, fcc and bcc phases.

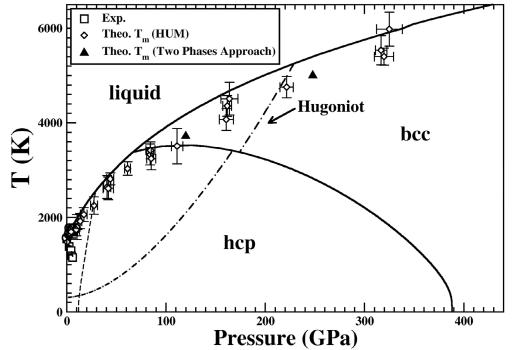
Instead of building our ion-thermal contribution from the elastic properties, which leads to the Debye model [4,5], we expressed the temperature dependence of the crystal quasi-harmonic free energy in terms of the log-moment ( $\theta_0$ ) and the mean-moment ( $\theta_l$ ) of the phonon density of states (PDOS) [14], as is more suitable for beryllium [1-3,6,7]:

$$F_l(\rho, T) = \frac{9}{8} k_B \theta_l(\rho) \quad (2)$$

$$+ 9k_B \left( \frac{T}{\theta_0(\rho)} \right)^3 \int_{\theta_0(\rho)/T}^{\infty} x^2 \ln(1 - e^{-x}) dx$$

where the first term is the phonon zero-point energy (ZPE).

Using full phonon spectrum for each phase, we find that neither the ZPE, nor the ion thermal contribution can stabilize the fcc or the R9 phases compared to the bcc and the hcp phases (not shown). The log-moment of R9 and fcc phases are nearly equivalent to that of hcp, and almost 50 K higher than for the bcc phase. As the R9 and fcc phases do not appear, we have to deal as usual with the hcp and the bcc phase and we propose the solid-phase diagram shown in Fig. 2. The hcp-bcc pressure transition at 0K is 390 GPa. We find that a variation of  $\pm 0.5\%$  on the log-moment leads to  $\pm 20$  GPa around this value. The melting curve borrowed from our previous QMD calculations [3] is shown only because it is needed for the thermoelasticity part (see below). With our model, beryllium undergoes a solid-solid phase change along the Hugoniot around 180 GPa and the hugoniot crosses the melt curve above 220 GPa.



**Figure 2.** Phase diagram of beryllium. The theoretical Hugoniot in the solid is also shown. The dashed line represents the 2.1 g/cc isochor.

## THERMOELASTICITY

It is customary in constitutive laws such as PTW to write the volume-temperature shear modulus as [8]

$$G(\rho, T) = G(\rho, T=0) \left( 1 - \alpha \frac{T}{T_m(\rho)} \right) \quad (3)$$

Here, the melting curve  $T_m$  comes from our QMD calculations. Throughout papers devoted to beryllium, only  $G(\rho, T=0)$  is discussed. The main point is that the *ab initio* calculations provide the monocrystal elastic constants, which can be averaged to obtain the polycrystalline shear modulus. For beryllium, different averaging models are not fully equivalent, especially in the bcc phase [4]. The Voigt-Reuss-Hill (VRH) average is considered here. The results of our calculation of the shear modulus at  $T = 0\text{ K}$  are not presented here and are similar to previous calculations [1,4,5].

Then for  $T > 0$ , it is necessary to take into account the dynamics of the ions. We follow two first-principles ways: QMD and DFPT calculations.

### a) QMD

The QMD calculations with 128 atoms/cell were previously performed in order to obtain the *ab initio* melting curve along 6 isochors. We select the data in the range of 0.8 to 1.0 times the melting temperature to calculate the mean square displacement, which is related to the -2-moment ( $\theta_2$ ) by

$$\langle u^2 \rangle_{QMD} = \frac{9\hbar^2 T_m(\rho)}{k_B M \theta_2^2(\rho, T_m)} \quad (4)$$

Then the -2-moment is converted to a -3-moment assuming that the ratio between the moments at  $T = 0\text{ K}$  and at  $T = T_m$  is a constant and that this constant is the same for all moments, which may be a crude approximation.

Using the Debye-solid relation  $\theta_D \sim G^{1/2} \rho^{-1/6}$  and taking  $G(\rho, T=0)$  and  $G(\rho, T=T_m)$  from Eq. (3), the temperature dependence  $\alpha$  of the shear modulus is given by

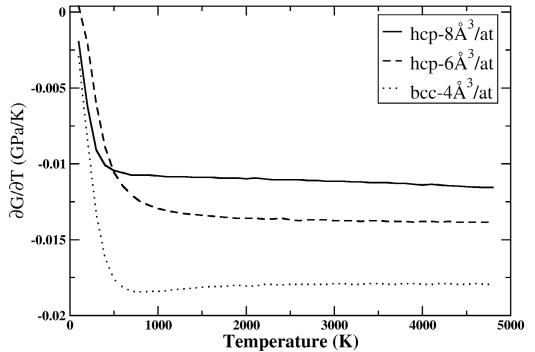
$$\alpha = 1 - \frac{G(\rho, T_m(\rho))}{G(\rho, 0)} = 1 - \frac{\theta_D^2(\rho, T_m(\rho))}{\theta_D^2(\rho, 0)} \quad (5)$$

We thus obtain for the two phases  $\alpha = 0.24 \pm 0.14$ . The uncertainties are mainly due the 10% temperature fluctuations in our NVE-simulations.

### b) DFPT

The lattice is distorted by applying a small strain on the parent lattice. The internal degrees of freedom are allowed to relax. Then, phonon calculations are performed. The entropy is extracted from the PDOS. So, we get the Helmholtz free energy as a function of volume and temperature. T. H. K. Barron and M. L. Klein [15] provided the strain-energy density.

For different magnitudes  $\delta$  of the strain, the total free energy difference between the distorted and undistorted lattices along an isotherm is fitted to a fourth order-polynomial form as a function of  $\delta$  and then equated to the appropriate elastic constant expression. Five and three independent strains are applied for hcp and bcc phases, respectively. The calculations are very time consuming so we only considered 3 volumes: 8, 6  $\text{\AA}^3/\text{at}$  in hcp and 4  $\text{\AA}^3/\text{at}$  in bcc. The temperature derivative of the VRH shear modulus is plotted Fig. 3. Due to the high Debye temperature, the asymptotic regime is reached only for  $T$  above 500 K.



**Figure 3.** Temperature derivative of the VRH shear modulus.

In the asymptotic regime, whatever the phase, an average value  $\alpha = 0.2 \pm 0.1$  can be proposed.

To take into account the low temperature behavior we propose the following fit considering the  $V = 6\text{ \AA}^3/\text{at}$  case as the average representative curve of the volumes studied,

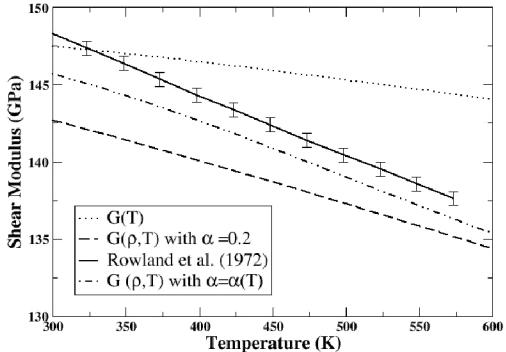
$$\alpha(T) = \frac{0.2}{\exp(0.009 * (356 - T)) + 1} \quad (6)$$

## DISCUSSION AND CONCLUSION

We now compare our results to experimental data [16] measured along an isobar. First we obtain the  $\rho$ - $T$  along an isobar using our equation of state. Then, we consider the following three approaches:

1. the VRH shear modulus at  $T = 0$ ,  $G_0(\rho)$  transformed to  $G(T)$  through  $\rho$ - $T$  relation.
2. the VRH shear modulus from Eq. (3) with  $\alpha = 0.2$
3. the VRH shear modulus from Eq. (3) with  $\alpha$  from Eq. (6).

Figure 4 presents results from these three cases together with experimental data. Proposition 3 matches rather well the experimental data and approaches the result for proposition 2 at high temperature.



**Figure 4.** Shear modulus-temperature diagram along the 1 bar isochor.

With both *ab initio* techniques we obtain  $\alpha = 0.24 \pm 0.14$ . This value is in good agreement with previous recommendations [9, 17]. We also find that the  $T$ -dependence of the shear modulus is independent of the phase. The non-asymptotic behavior (at temperatures below the Debye temperature) can also be handled.

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