Temperature-dependent elastic properties of α-beryllium from first principles

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Using density functional theory formulated within the framework of the exact muffin-tin orbitals method, we investigate the temperature dependence of the structural parameters and the elastic properties of the hexagonal closed-packed phase of Be (α-Be). We find that the elastic constants follow a normal behavior with temperature: decrease with increasing temperature with a slightly increasing slope. Up to the melting point, the monocrystalline elastic constants decrease by an average of 16% and the polycrystalline elastic constants by 10%. These trends contradict the large temperature factor observed in high-temperature direct pulse ultrasonic experiments. At the same time, the low-temperature pulse echo measurements confirm the present theoretical findings. Our results call for further accurate experimental studies on the elastic properties of α-Be at high temperatures.

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I. INTRODUCTION

Elastic constants of metals, in general, decrease smoothly and monotonically with increasing temperature, which can be described approximately by an empirical formula proposed by Wachtman *et al.*[1] As the elastic constants can be related to the long-wavelength limit of phonons, this normal behavior is due to anharmonic effects.[2] Anharmonicity causes thermal expansion, which affects the elastic constants through their volume dependence. However, in some metals, e.g., in Pd, Pt, Nb, V, and Ta,[3–7] the elastic constants vary anomalously with temperature, e.g., having local extrema. In most cases, anomalous contributions are explained by the structure of the electronic density of states in the vicinity of the Fermi level, which can be reached by thermal excitations.

In this work, we study the temperature-dependent elastic constants of hexagonal closed-packed (hcp) beryllium (α-Be). Because of its technological importance, this material has attracted notable interest during the past years, both from theory[8–13] and experiments.[14–16] Beyond its application in nuclear reactors as a highly effective moderator and reflector for neutrons, it is considered as a possible first wall material in future fusion reactors. Therefore, disclosure of the high-temperature elastic behavior of α-Be has a fundamental technological relevance.

Smith and Arbogast[17] have measured the elastic constants of α-Be between 75 and 300 K, applying pulse echo technique. They obtained an average change for the elastic constants $(\Delta C/\Delta T)_{av} = -0.009$ GPa/K. Contrary to their results, based on direct pulse ultrasonic measurements between 298 and 573 K, Rowland and White[18] found that the elastic constants of α-Be decrease on the average by 0.062 GPa/K. For comparison, in Mg the average change of the elastic constants measured for temperatures between 0 and 100 K (Ref. 19) and between 78 and 298 K (Ref. 20) is $(\Delta C/\Delta T)_{av,Mg} = -0.010$ GPa/K, whereas for Na $(\Delta C/\Delta T)_{av,Na} =$

-0.005 GPa/K in the 80–210 K temperature interval.[21] Therefore, the reported large temperature factor of the elastic constants of α-Be (Ref. 18) raises the possibility of their anomalous temperature dependence. Our aim is to investigate this question by calculating the elastic constants of α-Be as a function of temperature.

The paper is organized as follows. In Sec. II, we briefly overview the technique used in the theoretical determination of the temperature-dependent elastic constants. The computation method and numerical details are given in Sec. III. We present our results in Sec. IV, and in Sec. V, we discuss the present theoretical temperature dependence of the bulk modulus in comparison with available experimental data. The paper ends with conclusions.

II. THEORY

The isothermal elastic constants C_{ij} are derived from the second order strain derivative of the Helmhotz free energy $F = E_e + F_v - TS_e$ (Ref. 2), where E_e is the electronic energy, F_v is the phonon vibrational free energy, and S_e is the electronic entropy. Within the mean-field approximation, the electronic entropy is given by $S_e = -2k_B \int f(\epsilon) \ln f(\epsilon) + [1 - f(\epsilon)] \ln[1 - f(\epsilon)] N(\epsilon) d(\epsilon)$, where k_B is the Boltzmann constant, $f(\epsilon)$ is the Fermi-Dirac distribution, and $N(\epsilon)$ is the density of states. We use the Debye model to account for the main lattice vibration effects in the free energy. For the highly isotropic α-beryllium, this is a reasonable approximation.

In the total variation of the elastic constants, $\Delta C_{ij}(T,V) \equiv C_{ij}(T,V) - C_{ij}(T_0,V_0)$, where $V = V(T)$ is the equilibrium volume at T and $V_0 = V(T_0)$ is the equilibrium volume at $T_0 = 0$ K, we separate the constant-temperature $\Delta C_{ij}^T(T,V) \equiv C_{ij}(T,V) - C_{ij}(T,V_0)$ and the constant-volume $\Delta C_{ij}^V(T,V_0) \equiv C_{ij}(T,V_0) - C_{ij}(T_0,V_0)$ components. The temperature de-

pendence of $V(T)$ was determined from the Debye model as described, e.g., in Refs. 11 and 22.

To calculate the constant-temperature contribution, we make the approximation $\Delta C_{ij}^T(T,V) \approx \Delta C_{ij}^T(T_0,V)$, i.e., we neglect the temperature dependence of the phonon contribution. For a given temperature T and the corresponding volume $V(T)$, $\Delta C_{ij}^T(T_0,V(T))$ was obtained from the volume dependent elastic constants derived from the electronic energy $E_e(T_0,V)$. In order to get a smooth volume dependence, calculations were performed for seven different volumes between 26.72 and 58.79 bohr³. At each volume V, the theoretical hexagonal axial ratio $(c/a)_0$ was determined by minimizing the total energy $E_e(T_0,V,c/a)$ calculated for nine different c/a ratios close to the energy minimum. The hexagonal bulk modulus was obtained from a Morse function[23] fitted to the energy minima $E_e(T_0,V,(c/a)_0)$. The five hexagonal elastic constants, C_{11}, C_{33}, C_{44}, C_{12}, and C_{13}, were obtained from the bulk modulus, $B = [C_{33}(C_{11}+C_{12}) - 2C_{13}^2]/C_S$, where $C_S = C_{11}+C_{12}+2C_{33}-4C_{13}$, the logarithmic volume derivative of the hexagonal lattice parameter, viz. $d\ln(c/a)_0/d\ln V = -(C_{33}-C_{11}-C_{12}+C_{13})/C_S$, and three isochoric strains, as described in Ref. 24. In the isochoric distortions, the total energy was calculated for six different orthorhombic and monoclinic distortions ($\delta_{ort/mon} = 0.00, 0.01, \ldots, 0.05$) for $C_{66} = (C_{11}-C_{12})/2$ and C_{44}, respectively, and for nine hexagonal distortions ($\delta_{hex} = -0.04, -0.03, \ldots, 0.00, \ldots, 0.04$) for C_S. The constant-volume contribution $\Delta C_{ij}^V(T,V_0)$ was determined from the electronic free energy $F_e(T,V_0) = E_e(T,V_0) - TS_e(T,V_0)$ by calculating the five hexagonal elastic constants at V_0 for six different temperatures $T = 0, 300, 600, 900, 1200,$ and 1500 K.

III. COMPUTATIONAL METHOD

The present *ab initio* calculations are based on the density functional theory[25] using the generalized gradient approximation[26] for the exchange-correlation functional. This approximation proved to give more accurate bulk properties for α-Be than the local density approximation.[27] The Kohn-Sham equations[28] were solved using the exact muffin-tin orbitals (EMTO) method.[29–31]

The EMTO method is an improved screened Korringa-Kohn-Rostoker method,[31] where the full potential is represented by large overlapping muffin-tin potential spheres. By using overlapping spheres, one describes the crystal potential more accurately, when compared to the conventional muffin-tin or nonoverlapping approach.[30,32,33] Further details about this method can be found in Refs. 29–33. The EMTO approach has been applied successfully in the theoretical study of the elastic constants and phase stability of Fe-based alloys,[33–38] simple and transition metal alloys,[22,33,39,40] and Hume-Rothery systems,[30,33,41,42] as well as the crystal structure of complex oxides.[43–46]

The accuracy of the EMTO method for the equation of state of α-Be has been established by comparing the EMTO results with former full-potential data.[11] In particular, the equilibrium volume and bulk modulus obtained using present approach have been found to be in excellent agree-

TABLE I. Calculated and experimental elastic constants, Young (E), bulk (B), and shear (G) moduli (in GPa), and Poison ratios (ν) of α-Be at room temperature.

	EMTO	Expt.[a]	Expt.[b]
C_{11}	288.2	293.6	288.9±6.9
C_{33}	365.2	356.7	353.2±16.8
C_{44}	156.7	162.2	152.8±17.8
C_{12}	25.4	26.8	20.8±6.0
C_{13}	0.0	14.0	6.5±7.5
E	309.2	315.2	306.0±11.6
B	111.7	116.8	111.9±2.5
G	148.8	150.1	147.3±8.3
ν	0.039	0.050	0.039±0.018

[a]Reference 15.
[b]Mean values and experimental errors from Refs. 17, 18, 48–50, and 18.

ment with the theoretical results based on full-potential linear muffin-tin orbital[9] and pseudopotential[10] calculations. The accuracy of the EMTO method in the case of the hexagonal elastic properties of α-Be will be assessed in Sec. IV A.

In the self-consistent calculations, the one-electron equations were solved for s, p, and d orbitals within the scalar relativistic and soft core approximations. Including the Fermi-Dirac statistics explicitly in the EMTO calculations, we obtained temperature-dependent charge density, which was used to determine $E_e(T_0,V)$ and $F_e(T,V_0)$. The EMTO Green's function was calculated for 32 energy points. In the case of the strained structures, 53 550 k points were used in the irreducible part of the monoclinic Brillouin zones. The total charge density was expanded in spherical harmonics, including terms up to $l_{max} = 10$.

IV. RESULTS

A. Theory versus experiment

The calculated room temperature values of the elastic constants, Young (E), bulk (B), and shear (G) moduli, and Poisson ratios, together with the available experimental data, are listed in Table I. We find that all the present theoretical values agree with the measurements within the experimental errors. In Table I, we explicitly give the results of a recent measurement of Migliori *et al.*[15] Except for C_{13}, the elastic constants are in excellent agreement with this experiment: their differences are 2%–5%. We obtain a larger deviation for C_{13}. However, different measurements provide rather different values for this elastic constant. The Young, bulk, and shear moduli are in line with the measurements of Migliori *et al.*[15] within 4.5%, while the Poisson ratio is slightly underestimated in our calculations.

In addition to the elastic properties, we find that the room temperature equilibrium crystallographic unit-cell axial ratio, $(c/a)_0 = 1.5766$, agrees well with the recently measured[15] $c/a_{expt} = 1.568$: their difference being ~0.5%. We calculate
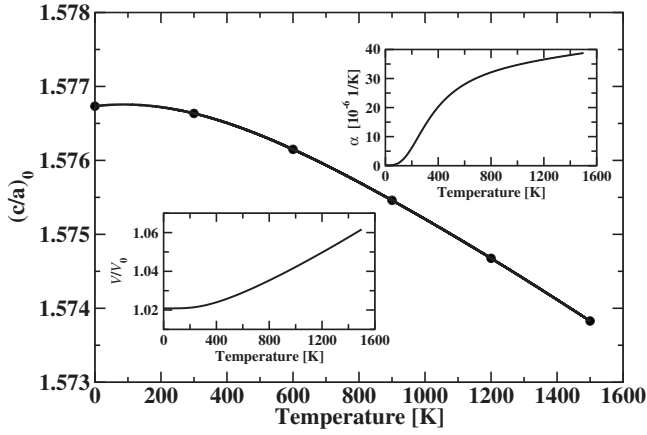
FIG. 1. The crystallographic unit-cell axial ratio $(c/a)_0$ of α-Be as a function of temperature. The relative volume and the linear thermal expansion coefficient (α) vs temperature are shown in the lower left and in the upper right insets, respectively.

1446.2 K for the Debye temperature at $T=300$ K, which deviates from the measured value ($\Theta_{D,\text{expt}}=1471$ K, Ref. [15]) by $\sim1.7\%$. Our room temperature linear thermal expansion coefficient, $\alpha=13.87\times10^{-6}$ 1/K, is also in line with the experimental value of $\alpha_{\text{expt}}=11.25\times10^{-6}$ 1/K[47]. Based on the above results, we conclude that the EMTO method accurately reproduced the experimental structural and elastic properties of α-Be. Therefore, we are confident that this approach can be used to study the temperature dependence of the elastic properties of hexagonal Be.

B. Effect of temperature on the crystal structure

The theoretical atomic volume of α-Be follows a normal behavior with increasing temperature (Fig. 1, left inset). Between 0 and 1500 K, $V(T)$ increases by $\sim6\%$, including the $\sim2\%$ increase due to the zero-point vibration. Accordingly, the thermal expansion coefficient of α-Be (Fig. 1, right inset) is about half of those of other alkaline earth metals. The equilibrium hexagonal axial ratio has also been determined as a function of temperature (Fig. 1). It is found that $(c/a)_0(T)$ slightly decreases with temperature. Its variation is about -0.2% as the temperature changes from 0 to 1500 K. Due to the small change in $(c/a)_0$, the thermal expansion
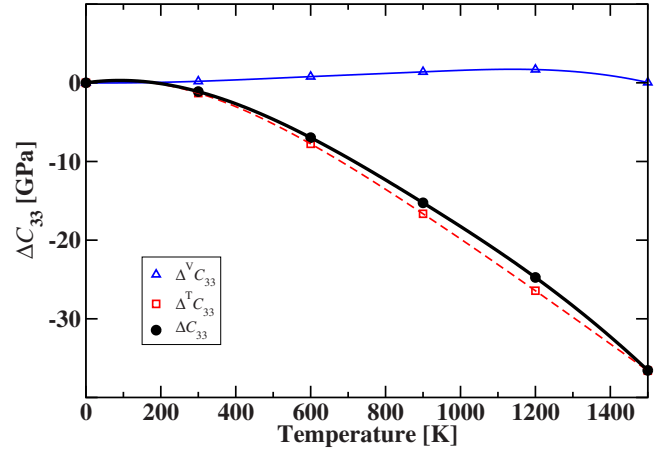

FIG. 2. (Color online) The calculated temperature dependence of the C_{33} elastic constant of α-Be. $\Delta^V C_{33}$ (triangles) denotes the electronic component, while $\Delta^T C_{33}$ (squares) stands for the thermal expansion component. ΔC_{33} displays the total variation (circles). The curves are cubic splines fitted to the calculated values.

coefficients in the basal plane and along the hexagonal c axis are practically identical. This indicates that α-Be is to a good approximation isotropic, and the anisotropy parameters[11] show negligible ($\lesssim0.4\%$ below 1500 K) temperature dependence.

C. ΔC^T and ΔC^V terms

In Table II, we give the volume dependence of the hexagonal elastic constants and bulk modulus calculated using the EMTO method. We can observe that all elastic constants decrease significantly with increasing volume. The $C_{ij}(V)$ curves from Table II along with the $V(T)$ curve from Fig. 1 are used to establish the constant-temperature contribution $\Delta C_{ij}^T(T_0,V)$ to the temperature dependence of the elastic constants.

In Fig. 2, we compare the calculated electronic ($\Delta^V C_{ij}$) and the thermal expansion ($\Delta^T C_{ij}$) contributions to the temperature dependence of the C_{33} elastic constant of α-Be. We find that the constant-volume term, $\Delta^V C_{33}$, does not change notably with the temperature. Its average variation in the whole temperature interval (0–1500 K) is $\Delta C_{33}^V/\Delta T=0.0005$ GPa/K. We obtain similar results for the other four

TABLE II. Elastic constants and bulk modulus (B) of α-Be (in GPa) at different volumes (in atomic units) and zero temperature. ($B=[C_{33}(C_{11}+C_{12})-2C_{13}^2]/C_S$, where $C_S=C_{11}+C_{12}+2C_{33}-4C_{13}$.)

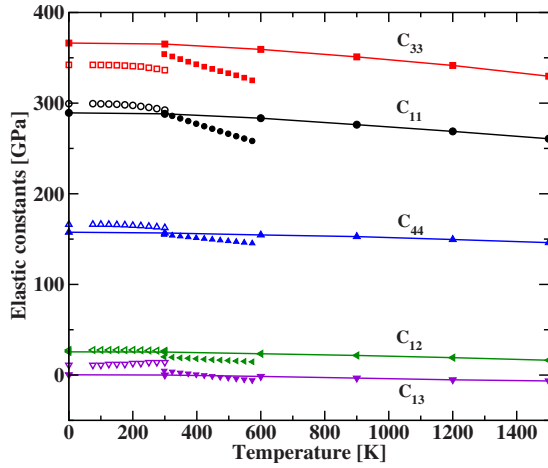| V	C_{11}	C_{33}	C_{44}	C_{12}	C_{13}	B
26.72	1373.34	1817.88	443.09	661.18	320.94	796.19
32.07	970.14	1258.23	346.61	385.80	182.39	521.68
37.41	700.26	894.94	280.76	231.89	105.39	352.97
42.76	525.00	662.82	241.49	137.59	52.00	243.66
48.10	397.13	506.33	197.25	73.57	21.73	169.99
53.45	304.81	387.06	163.23	31.89	3.59	118.83
58.79	239.64	299.89	140.13	8.43	-12.61	82.46

FIG. 3. (Color online) Calculated (filled symbols and lines) and experimental elastic constants as a function of temperature. The experimental data of Smith and Arbogast (Ref. 17) are denoted by open symbols, while those from the measurements of Rowland and White (Ref. 18) are displayed with filled symbols.

elastic constants as well. Their average changes are $\Delta C_{11}^V/\Delta T=-0.0008$, $\Delta C_{44}^V/\Delta T=-0.0009$, $\Delta C_{12}^V/\Delta T=0.0007$, and $\Delta C_{13}^V/\Delta T=-0.0005$ GPa/K. Consequently, the contribution of $\Delta^V C_{ij}$ to the total variation of elastic constants is practically negligible. The explanation to this effect is given in Sec. V. Figure 2 also demonstrates that it is the thermal expansion or constant-temperature term that essentially determines the total variation of the elastic constants with temperature. That is, according to our results, the main temperature factor of C_{ij} appears through the volume change.

D. Temperature dependence of C_{ij}

Our calculated elastic constants for α-Be, as well as the corresponding experimental data by Smith and Arbogast[17] and by Rowland and White,[18] are shown in Fig. 3 as a function of temperature. Considering the theoretical results, we find that C_{33} decreases to the largest extent in the whole temperature range: 36.6 GPa, followed by C_{11} with 28.5 GPa. C_{44}, C_{12}, and C_{13} decrease by 11.5, 9.2, and 6.8 GPa, respectively. We note that the theoretical C_{13} becomes negative above ~300 K, which is in qualitative agreement with experiment.[18] The theoretical curves from Fig. 3 indicate that the elastic constants of α-Be follow a normal behavior with temperature.

Figure 3 illustrates that our theoretical elastic constants are relatively close to the measurements of Smith and Arbogast[17] in the 0–300 K temperature range. However, we obtain significantly larger deviations between theory and the experimental data of Rowland and White.[18] Our average change of elastic constants in the temperature range of their measurements is -0.011 GPa/K, which is about one-sixth of their average variation (-0.062 GPa/K).

V. DISCUSSION

The large discrepancy between the present results from Fig. 3 and those reported by Rowland and White[18] calls for
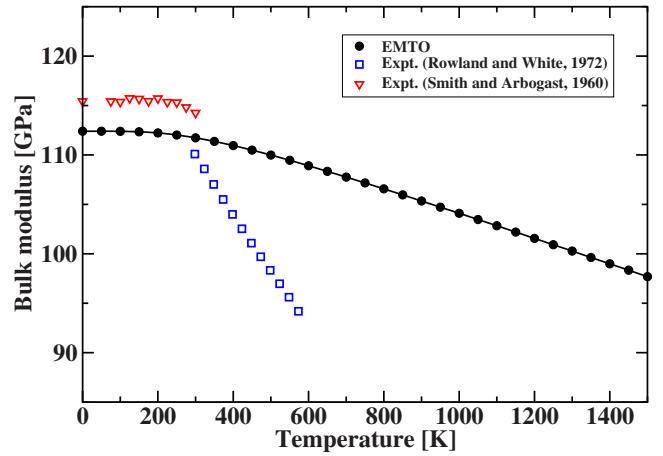

FIG. 4. (Color online) Calculated (circles) and measured bulk moduli as a function of temperature. Experimental data are taken from Ref. 18 (squares) and Ref. 17 (triangles).

further investigations to establish whether the theoretical or the experimental results are closer to the true temperature dependence of the elastic constants of α-Be. To this end, we select the bulk modulus and carry out a thorough comparison between the existing experimental and theoretical data.

In Fig. 4, we compare the present theoretical temperature-dependent bulk modulus to the available experimental values. As expected, we obtain a significant deviation from the experiment by Rowland and White,[18] who derived the bulk modulus from the measured elastic constants. They obtained a linear trend with an average change $\Delta B/\Delta T\approx-0.058$ GPa/K. In the same temperature interval, we calculate less than one-sixth (-0.009 GPa/K) of that. On the other hand, between 0 and 300 K, we obtain $\Delta B/\Delta T=-0.002$ GPa/K, which is in excellent agreement with the average variation of -0.003 GPa/K derived from the measurements of Smith and Arbogast.[17]

Our results are also confirmed by the recent theoretical study of Song and Liu.[13] These authors calculated the bulk modulus of α-Be to be between 0 and 1400 K using projected augmented wave method[51] and mean-field potentials.[13] Between 300 and 600 K, i.e., in the temperature interval of the experiments of Rowland and White,[18] Song and Liu obtained $\Delta B/\Delta T=-0.008$ GPa/K, which is very close to our value. Furthermore, we note that at 1400 K, the present theoretical bulk modulus (98.99 GPa) agrees within the numerical accuracy, with 98.75 GPa obtained by Song and Liu for the same temperature.

In this discussion, we should keep in mind that the experimental temperature factor between ~300 and ~600 K (Ref. 18) would suggest an unusually soft high-temperature Be. If we assume a linear variation for $B(T)$ with T (Refs. 1 and 2) and extrapolate the experimental bulk modulus of Rowland and White[18] to high temperature, we get $B_{\text{extrapolated}}\sim40$ GPa at 1500 K. This would lead to a hcp phase that is much softer than the body centered cubic (bcc) phase, and would make the experimentally observed hcp$\rightarrow$bcc phase transition at 1530 K very unlikely.

Next, we examine the possibility of an anomalous temperature dependence of the elastic constants on the grounds
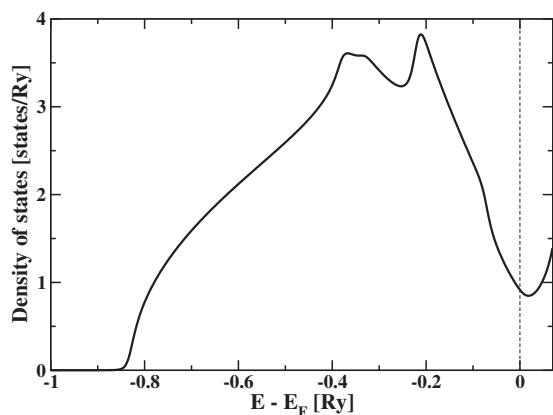
FIG. 5. Calculated density of states of α-Be at the equilibrium volume. The Fermi level (E_F) is denoted by a vertical dashed line.

of the electronic structure. We calculated the total density of states $[\mathcal{D}(E)]$ of α-Be at its equilibrium volume. In this calculation, we used $\sim 10^5$ k points in the irreducible Brillouin zone in order to produce an accurate $\mathcal{D}(E)$ curve near the Fermi level (E_F). Figure 5 shows $\mathcal{D}(E)$ as a function of energy. As we can see, the density of states is smooth near E_F. The closest structure in $\mathcal{D}(E)$ appears at $|E-E_F| \gtrsim 0.03$ Ry, corresponding to temperatures of the order of thousands of Kelvin. Consequently, in α-Be the anomalous temperature dependence coming from electron excitations can safely be ruled out.

The comparisons above indicate that the discrepancy between theory and experiment from Figs. 3 and 4, to a large extent, comes from the inaccuracy of the experimental data. One possible reason for that may be the presence of impurities in the Be crystals used in the experiments.[18] The Be samples measured by Rowland and White were cut from large grained cast ingots, and contained Al, Fe, Si, and O as

the major contaminants.[18] Among the possible impurities in α-Be, the vacancies may have a significant effect on the elastic properties. Using the present computational approach, we have examined the effect of vacancies on C_{66}, for which the largest deviation between experiment and theory was obtained. We have found that C_{66} decreases by ~ 1452 GPa per vacancy concentration. This effect is very large and could partly account for the obtained discrepancies. However, the theoretical vacancy formation energy in pure α-Be is ~ 0.8 eV,[12] which keeps the concentration of thermal vacancies at a rather low level at temperatures of interest. We mention that the thermodynamics of vacancies and of other possible defects in the presence of chemical impurities is not known at the present.

VI. CONCLUSIONS

We have studied the temperature dependence of the structural parameters and the elastic constants of α-Be. In contradiction to what could be expected from a formal systematic experimental study,[18] we have found that the elastic constants follow a normal behavior with temperature. We have demonstrated that α-Be remains nearly isotropic up to the melting temperature of ~ 1500 K. Our results support the weak temperature factor observed in a pulse echo measurement.[17] Our results necessitate new experimental investigations on the temperature dependence of the elastic constants in α-Be in the high-temperature region.

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