Origin of bcc to fcc phase transition under pressure in alkali metals

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Abstract. The electronic, dynamical and elastic properties of body-centered cubic (bcc) alkali metals (Li, Na, K, Rb and Cs) at high pressure are extensively studied to reveal the origin of the phase transition from bcc to face-centered cubic (fcc) by using ab initio calculations. The calculated 3D Fermi surface (FS) shows an anisotropic deformation by touching the Brillouin zone boundary at the N point with pressure for Li, K, Rb and Cs due to the s → p and s → d charge transfers, respectively. However, no clear charge transfer is found in Na, in favor of an isotropic FS even at very high pressure. The traditional charge transfer picture and the newly proposed Home–Rothery model in understanding the bcc → fcc transition are thus questionable in view of their difficulties in Na. In this paper, a universal feature of pressure-induced instability of the tetragonal shear elastic constant $C'$ and the softening of the transverse acoustic phonons along the [0ξξ]-direction near the zone center for all the alkali metals is identified. Analysis of the total energy results suggests that $C'$ instability associated with the soft mode is the driving force for the bcc → fcc transition, which could be well characterized by the tetragonal Bain’s path.

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1. Introduction

The properties of materials at high pressure arouse great interest in connection with the possibility of obtaining new phases with uncommon properties as well as for geophysical and astrophysical applications. In high-pressure studies, the alkali metals have attracted much attention due to the variety of physical phenomena occurring under compression, such as remarkably increased electrical resistivities [1], enhanced superconductivities [2] and unusually low melting temperatures [3]. Under ambient conditions, the interaction between valence electrons and ionic cores in the alkali metals is weak and the nearly free electron model has been considered as a good approximation to describe their physical properties [4]. However, recent experimental high-pressure diffraction investigations [5]–[14] of the alkali metals have revealed surprising and interesting results. Alkali metals, adopting the body-centered cubic (bcc) structure at ambient pressure, exhibit complex and low coordination structures at high pressure and have one of the most complex phase-transition sequences among element solids [5]–[9]. Li, Na, K, Rb and Cs were observed to transform to face-centered cubic (fcc) structure at pressures of 7 GPa [10], 65 GPa [6], 11.5 GPa [15], 7 GPa [11] and 2.3 GPa [12], respectively. At higher pressure, all alkali metals transform into more complex structures [5]–[7], [9], [12]–[14]. The complex transformations are understandable by the analysis of Fermi surface (FS) nesting with the phonon softening along the $\Gamma X$ direction occurring in the fcc structure upon compression [16].

There are many theoretical investigations related to the understanding of bcc $\rightarrow$ fcc phase transitions in the alkali metals. It has been found that as a result of the increased overlap of the valence wavefunctions, the delocalized s-valence electrons transfer to the more localized d electrons in K, Rb, and Cs [17, 18], and p electrons in Li [18]–[20] upon compression. Although these electronic changes have been considered as the driving force of the bcc $\rightarrow$ fcc phase transitions in Li, K, Rb and Cs [17]–[20], the charge transfer mechanism in Na is very difficult to understand. Very recently, the stability of bcc Li [21] has been analyzed within the Home–Rothery mechanism [22]. It was suggested that the interaction between the FS and Brillouin zone (BZ) boundary could open up a pseudogap and then reduce the overall electronic energy, thus resulting in a structural phase transition. However, since the electronic structure of Na shows negligible changes with increasing pressure [16, 23], the Home–Rothery model also fails to uncover the driving force of the bcc $\rightarrow$ fcc transition in Na. Therefore, it is suggested that the earlier theoretical studies focusing only on the changes of the electronic structure could not reveal the physical mechanisms beneath the bcc $\rightarrow$ fcc transitions in all the alkali metals.
It is known that dynamical instabilities [24] are often responsible for phase transitions under pressure. Earlier, two theoretical works for bcc Cs [25] and Li [21], reported the transverse acoustic (TA) phonon softening along the [0ξξ]-direction near the zone center and considered this softening as the possible driving force for the bcc → fcc transition. However, the lack of detailed transition path related to the phonon softening precludes us from fully understanding the phase transformation. The elastic properties define the behaviors of a material that undergoes stress, deforms, and then recovers and returns to its original shape after stress ceases. Thus, the elastic behaviors might also play an important role in driving the structural changes. In this paper, we present a systematic study on the electronic structures, lattice dynamics and elastic constants of bcc alkali metals as a function of pressure to probe the physical origin of the bcc → fcc transition. We found that the transitions are driven by the instabilities of the tetragonal elastic constant \( C' \) associated with the TA phonon softening along the [0ξξ]-direction near the BZ center. The tetragonal Bain’s transition paths are thus proposed in terms of the \( C' \) instabilities and supported by the total energy calculations.

2. Method of calculation

Ab initio calculations of the bcc alkali metals were performed in the framework of the density functional theory (DFT) [26] within the generalized gradient approximation (GGA) [27]. The total energy, density of states (DOS), and FS calculations were carried out by using the full-potential linear augmented plane-wave (FP) method, through WIEN2K [28]. The value of \( R_{MT}K_{\text{max}} \) (the smallest muffin-tin radius multiplied by the maximum \( k \) value in the expansion of the plane wave in the basis set) which determines the accuracy value of the basis set used is set to be 9. Convergence tests gave the use of 8000 \( k \)-points for the self-consistent calculation in the BZ. A large set of 32 768 \( k \)-points was employed in the calculation of the FS and the electronic DOS. In all the calculations, self-consistency was achieved with a tolerance of 0.1 mRy in the total energy.

In an effort to obtain reliable theoretical results, the lattice dynamics calculations are performed in two different computational approaches: the linear response method within the density functional perturbation theory (DFPT) [29] and the direct supercell calculation (SC) method [30]. The linear response calculation is performed by using the pseudopotential plane-wave (PP) method through the Quantum-ESSPRESSO code [31]. The Troullier–Martins [32] norm-conserving scheme is used to generate the pseudopotentials for Li, Na, K, Rb and Cs, respectively. A nonlinear core correction to the exchange-correlated energy functional was introduced to generate pseudopotentials for Li and Na. Instead, 3p, 4p and 5p semicore states are incorporated into the valence electrons for K, Rb and Cs, respectively. Convergence tests gave a kinetic energy cutoff \( E_{\text{cutoff}} \) as 80 Ry and a \( 20 \times 20 \times 20 \) Monkhorst–Pack (MP) [33] grid for the electronic BZ integration. A \( 20 \times 20 \times 20 \) MP \( k \) mesh was found to yield phonon frequencies converged within 0.05 THz. An \( 8 \times 8 \times 8 \) MP \( q \) mesh in the first BZ was used in the interpolation of the force constants for the phonon dispersion curve calculations. The direct supercell method is implemented in the PHON program [34]. This method uses the Hellmann–Feynman forces calculated from the optimized supercell through the Vienna ab initio simulation package (VASP) [35]. Electron–ion interaction was represented by the projector augment wave (PAW) method [36], which fully treats all the electrons. Convergence check gave the use of a \( 4 \times 4 \times 4 \) supercell containing 64 atoms in the force constant calculation. The choices of a \( 4 \times 4 \times 4 \) MP \( k \) mesh in the BZ and a plane-wave cutoff of 800 eV converge the total
energy to be better than 1–2 meV per atom. Elastic constants were obtained from evaluations of the stress tensor generated by small strains using VASP. The integration in the BZ was done by using a $24 \times 24 \times 24$ MP $k$ mesh.

3. Results and discussion

The theoretical equilibrium lattice constants and equation of states (EOS) of the bcc structure for the alkali metals were determined by fitting the total energies as a function of volume to the third-order Birch–Murnahan EOS [37]. The calculated equilibrium lattice parameters ($a_0$), bulk modulus ($B_0$) and the pressure derivative ($B_0'$) within the FP, PP and PAW methods together with other theoretical results [6, 25, 38, 39] and the experimental data [6, 10], [40]–[42] are listed in table 1. The theoretical lattice constants are found to be in good agreement with the experimental data within 2.1, 2.5, 2.0, 1.0, and 0.6% for Li, Na, K, Rb and Cs, respectively. The satisfactory agreement strongly supports the GGA approximation for this study. The calculated EOS of the alkali metals within FP, PP and PAW methods are compared with the experimental data [6, 40, 41, 43] as shown in figure 1. The agreement between the theoretical results and the experimental data is excellent, supporting the validity of the current theoretical models with the presence of pressure. It is noteworthy that the excellent mutual agreement within the choices of the FP, PP and PAW methods verifies the consistency of the use of three different \textit{ab initio} methods.

An essential feature determining the electronic properties of any metal is the FS topology. Figure 2 shows the three-dimensional (3D) FS of the bcc alkali metals at the selected pressures. It is clear that at ambient pressure the 3D FSs for all the alkali metals are nearly perfectly spherical resulting from the nearly free electron character. With increasing pressure, except for that in Na, the FSs are found to become highly anisotropic and start touching the BZ boundary at the $N$ point at 7, 10, 5 and 1 GPa for Li, K, Rb and Cs, respectively. Notably, at higher pressure, the FSs of K, Rb and Cs show an intriguing feature of increased necks along the $\Gamma N$ direction. It was previously suggested [22] that the interaction between the FS and the BZ boundary could open up a pseudogap along the $\Gamma N$ direction and then reduce the overall band-structure (electronic) energy, which can be understood as the Hume–Rothery model. Therefore, it was proposed that the instability of the electronic structure with pressure might be related to the observed structural phase transitions in the bcc Li, K, Rb and Cs. However, the Hume–Rothery model has a major difficulty in understanding the transition of Na (figure 2(b)), where an electronic instability is apparently absent.

To understand the FS topological changes with pressure, we plotted the angular momentum-decomposed DOS divided by total DOS at the Fermi level as a function of pressure in figure 3. From figure 3(a), one observes that the Li 2p contribution is already significant (72%) even at zero pressure and increases steadily at the expense of decreasing 2s character. As the 2p states are located just above the Fermi level for Li, the $s \rightarrow p$ transitions lower the motion of the 2p band and move it below the Fermi level resulting in the touching of FS at the $N$-point of the BZ boundary. For Na (figure 3(b)), it is shown that at zero pressure, the 3s and 3p electrons dominate the total DOS, while the 3d contribution is very small (8%). With increasing pressure, the 3s decreases and the 3d increases slightly but remains small (about 12% at 120 GPa), whereas the 3p stays almost constant at 55% when the pressure is larger than 30 GPa. This fact is the main cause for the persistence of the spherical FS in Na at high pressure even up to 120 GPa. From figure 3(c)–(e), it is important to note that the d contribution of the heavier alkali metals...
Table 1. Calculated equilibrium lattice parameters ($a_0$), bulk moduli ($B_0$) and the pressure derivatives of the bulk moduli ($B_0'$) for bcc Li, Na, K, Rb and Cs, respectively. Previous theoretical data from [6, 25, 38] and [39] and the experimental data from [6, 10] and [40]–[42] are also listed for comparison.

| Alkali metals | $a_0$ (au) | $B_0$ (GPa) | $B_0'$ |
|---------------|------------|-------------|--------|
| Li            |            |             |        |
| FP            | 6.49       | 13.33       | 3.62   |
| PP            | 6.54       | 13.47       | 2.68   |
| PAW           | 6.51       | 16.00       | 2.53   |
| Dacorogna and Cohen [38] | 6.41 | 13.28       | 2.84   |
| Experiment    | 6.63$^a$   | 11.32$^a$   | 3.62$^a$ |
| Na            |            |             |        |
| FP            | 7.91       | 8.35        | 3.79   |
| PP            | 7.94       | 8.10        | 2.84   |
| PAW           | 8.02       | 8.54        | 2.72   |
| Hanfland et al [6] | 7.98 | 6.81        | 3.93   |
| Experiment    | 8.11$^b$   | 6.31$^b$    | 3.89$^b$ |
| K             |            |             |        |
| FP            | 10.00      | 3.68        | 3.66   |
| PP            | 9.87       | 4.30        | 2.79   |
| PAW           | 10.03      | 6.08        | 1.87   |
| Dacorogna and Cohen [38] | 9.67  | 4.10        | 3.80   |
| Experiment    | 10.07$^c$  | 2.96$^c$    | 4.06$^c$ |
| Rb            |            |             |        |
| FP            | 10.79      | 2.84        | 3.52   |
| PP            | 10.84      | 3.50        | 2.20   |
| PAW           | 10.67      | 3.35        | 2.10   |
| Sigalas et al [39] | 10.21 | 3.50        | 3.90   |
| Experiment    | 10.78$^c$  | 2.30$^c$    | 4.10$^c$ |
| Cs            |            |             |        |
| FP            | 11.50      | 2.29        | 3.17   |
| PP            | 11.60      | 1.81        | 2.40   |
| PAW           | 11.66      | 2.17        | 2.34   |
| Xie et al [25] | 11.39  | 2.20        | 4.87   |
| Experiment    | 11.67$^d$  | 2.30$^e$    |        |

$^a$Olinger and Shanen [10].
$^b$Hanfland et al [6].
$^c$Winzenick et al [40].
$^d$Takemura et al [41].
$^e$Swenson [42].

K, Rb and Cs increases rapidly with increasing pressure. The d contribution starts to dominate the total DOS at 10, 5 and 1 GPa for K, Rb and Cs, respectively, which are consistent with the pressures at which the FS touches the BZ boundary. Therefore, the $s \rightarrow d$ electron transitions are suggested to be responsible for the FS deformation in the three heavy alkali metals. Interestingly, by examining the band structures of K, Rb and Cs, we found that the position of the unoccupied
d band drops closer to Fermi level as the atomic number becomes larger at zero pressure. This finding is attributed to the fact that the touching pressure decreases as the atomic number increases among the heavy alkali metals. Note that our calculation of partial DOS for Li, Na, K, Rb and Cs is in excellent agreement with the calculations by Shi and Papaconstantopoulos [44].

Figure 4 shows the comparison of the theoretical phonon dispersion curves calculated by the DFPT and SC approaches with the experimental inelastic neutron scattering data [45]–[49] for the bcc alkali metals at ambient conditions. It is found that the two results are in excellent agreement with the experimental data (deviations $\leq 5\%$) for Na, K, Rb and Cs, except for Li with somewhat larger deviations of 15% along the $[\xi\xi\xi]$-direction. Note also that the present results are in good agreement with those of Frank et al [30] for bcc Li, Na and K. The overall good agreement in phonons among the current results, the available experimental data, and other calculations at zero pressure gives us confidence to explore the high pressure properties.

The phonon spectra as a function of pressure are shown in figure 5. Here, we only show the phonon spectra along the $\Gamma N$ high symmetry directions where the pressure-induced phonon instabilities occur. The left and right panels present the calculated phonon frequencies by using the DFPT and the SC methods, respectively, where $-|\nu|$ is plotted when $\nu^2(q) < 0$. To obtain very accurate phonon dispersion in the DFPT method, phonon frequencies at the individual

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**Figure 1.** Comparison of the calculated equation of states (solid line) for bcc Li (a), Na (b), K (c), Rb (d) and Cs (e) with the experimental data (solid square symbols). The black solid lines are the results from the FP method, the red dashed lines from the PP method and the blue dotted lines from the PAW method.
Figure 2. FSs of bcc Li (a), Na (b), K (c), Rb (d) and Cs (e) at the selected pressures.

$q$-points along the $[0ξξ]$-direction were explicitly calculated to eliminate possible interpolation errors. The phonon frequencies calculated by the two approaches show excellent mutual agreement, validating the current calculations. It is clear that a similar TA phonon softening along the $[0ξξ]$-direction is predicted for all the bcc alkali metals. The imaginary TA phonons
Figure 3. The calculated angular momentum-decomposed DOS divided by total DOS at the Fermi level for bcc Li, Na, K, Rb and Cs with pressure using the FP method. The dashed line indicates the pressure where bcc to fcc phase transition occurs in the experiments.

were found at the pressures 4, 80, 15, 8 and 2.3 GPa for Li, Na, K, Rb and Cs, respectively, signaling a structural instability. The softening behaviors agree well with those previously reported in [21] for Li and in [25] for Cs. It is worth noting that in contrast to Li, K, Rb and Cs, the zone edge instability at the $N$-point is solely found for Na. This might be originated from its unique charge transfer behavior. Nevertheless, a phonon softening at the zone center along the $\Gamma N$ direction is also evidenced in Na, similar to other alkali metals.

A comparison of the calculated elastic constants with experimental data [47, 50], [53]–[55] and the previous theoretical results [25, 51, 52, 55] at ambient pressure for the bcc alkali metals is given in table 2. It is found that our calculation results are in good agreement with the experimental data and the previous theoretical calculations. The variations of the tetragonal shear $C'$ and trigonal shear $C_{44}$ with pressure are presented in figure 6. The current results are found to compare well with the other theoretical calculations for Li [52], Na [56] and K [56].

It is worth recalling that the slopes of phonon dispersions at $q \rightarrow 0$ are related to the elastic constants of a material. For a bcc solid, when $q \rightarrow 0$ is along the $[\xi \xi 0]$-direction a formula of $\rho u_T^2 = (C_{11} - C_{12})/2$ validates, where $\rho$ is the atomic density, $u_T = d\omega_T/dq$,
$\omega_T = 2\pi v_T$ ($v_T$ is the TA phonon frequency). Therefore, the tetragonal shear elastic constant $C' = (C_{11} - C_{12})/2$ is strongly related to the long-wavelength part of the transverse branch along $[\xi\xi0]$. With the above consideration, one can easily understand the variation of $C'$ with the pressure (figure 6). It is found in figure 6 that $C'$ softens with pressure for Li, but first increases then drops for Na, K, Rb and Cs. These behaviors can be well understood by the pressure dependences of the phonons shown in figure 6. It is evidenced that Li phonons decrease linearly to become imaginary, but the phonons first harden and then soften in Na, K, Rb and Cs. Moreover, $C'$ was found to become negative at the pressures 4, 100, 15, 8 and 2.3 GPa for Li, Na, K, Rb and Cs, respectively. These pressures agree perfectly with the pressures of zone center phonon softening being imaginary. With the above analysis, it is suggested that the softening of the shear constant $C'$ is associated with the TA phonon softening along the $[\xi\xi0]$-direction. It is noteworthy that although $C_{44}$ also has a trend of decreasing with pressure, it remains positive in the studied pressure range. Since $C'$ is negative, the alkali metals within the bcc structure become elastic unstable at high pressure.
Figure 5. Calculated TA phonon frequencies of bcc Li (a), Na (b), K (c), Rb (d), and Cs (e) along the [0ξξ]-direction with pressure (frequencies below zero denote imaginary values). The left and the right panels are the results from the DFPT and SC methods, respectively.

The strain stress corresponding to the $C'$ shear modulus in the calculation is defined as

$$\varepsilon_{\text{tetra}} = \frac{1}{3} \begin{pmatrix} -\delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & 2\delta \end{pmatrix}$$

and the energy difference between the original and distorted structures is

$$\Delta E_{\text{tetra}} = \frac{1}{4}(C_{11} - C_{12})\delta^2 + O(\delta^3).$$

This distortion modifies the $a$-, $b$-, and $c$-axes but keeps $a$ and $b$ the same. A consequence of the $C'$ instability is a transition from the bcc to a body-centered tetragonal (bct) structure. Notably, both the bcc and fcc structures can be described as bct structures. In the bcc structure, all three lattice vectors have equal length $a$, whereas in the fcc cases $a$ and $b$ are equal and the lattice-axis $c$ has the length $\sqrt{2}a$. Figure 7 shows a schematic representation of the bcc and fcc.
structures assuming a common bct. Thus, the bcc → fcc transformation can be described by the tetragonal Bain’s path [55, 57, 58], a continuous change of the single variable, $c/a$ ratio, from 1 to $\sqrt{2}a$. Figure 8 presents the total energy $E$ as a function of $c/a$ ratios at the selected pressures. It is evident that at zero pressure, all the $E(c/a)$ curves exhibit double well features with two minima located at $c/a = 1$ and $c/a = \sqrt{2}$, respectively. Interestingly, the fcc structure is found to be more energetically favorable than the bcc structure at zero pressure and temperature. The energy difference between the bcc and fcc structures is 2.18, 0.693, 0.318, 0.731 and 0.789 meV for Li, Na, K, Rb and Cs, respectively. This fact is in excellent agreement with experimental [59] and earlier theoretical [39, 55] works. However, at room temperature, it has been experimentally demonstrated that the bcc structure is stable at ambient conditions and transforms into the fcc structure upon compression. To reveal the phase transition mechanism of bcc to fcc in the alkali metals, we have assumed that the bcc structure is the stable structure even at a low temperature. The validity of this assumption has been justified by a well-defined total energy double well as shown in figure 8 to clearly characterize the first-order phase transition. Also, the 300 K temperature effects on the simulated phonons or elastic constant are expected to be very small. Thus, the only slightly higher total energy in the bcc structure will not affect our discussion and the final conclusion. With increasing pressure, the local minima at $c/a = 1$ disappear at 6, 105, 15, 8 and 2.3 GPa for Li, Na, K, Rb and Cs, respectively, and those located at $c/a = \sqrt{2}$ dominate. As a result, the bcc structure is no longer favorable at high pressure for all the alkali metals. Instead, a transition to fcc structure is overwhelmingly preferred. To support the stability of the fcc structure further, we calculated the elastic constants and enthalpies at these pressures and compared with those in the bcc structure as listed in table 3. Indeed, under these pressures, the fcc structure is both dynamically and thermodynamically stable.
Based on the current studies, we have predicted the TA phonon softening along [ξξξξ0] and shear elastic modulus C' instability for the bcc alkali metals under pressure. Although the predicted phase transition pressures corresponding to these instabilities are higher (for Na, K and Rb) or lower (for Li) than the experimental data, the common features of the soft mode and elastic instability are quite clear and could be used to understand the phase transition mechanism. Even if the bcc → fcc transition is first-order, the phonon softening or elastic instability acting as a phase transition driving force is evidenced. From the Landau theory, an independent soft phonon or elastic instability-induced phase transition renders a second-order nature. Soft phonon or elastic instabilities could also drive a first-order phase transition, but the coupling of the strain and phonon modes becomes significant [60]. In particular, a universal pressure-induced softening behavior of the shear constant and TA phonon mode is identified for all the alkali metals. Therefore, the current theory strongly indicates that the physically driven mechanism of the bcc to fcc phase transition in alkali metals is originated from the C instability coupled with the TA phonon softening along the [0ξξξξ]-direction and the transitions follow the Bain’s path as supported by the total energy calculation.

Table 2. Calculated elastic constants of C_{11}, C_{12}, C' and C_{44} for the bcc alkali metals at ambient pressure. Earlier theoretical results from [25], [51, 52] and [55] and the experimental data from [47] and [50], [53]–[55] are also shown for comparison.

|     | C_{11} (GPa) | C_{12} (GPa) | C_{44} (GPa) | C' (GPa) |
|-----|-------------|-------------|-------------|---------|
| Li  | This work   | 13.15       | 12.00       | 10.75   | 0.57    |
|     | Mehl [52]   | 15.60       | 14.80       | 11.10   | 0.80    |
|     | Experiment  | 13.94\textsuperscript{a} | 11.69\textsuperscript{a} | 10.69\textsuperscript{a} | 1.12\textsuperscript{a} |
| Na  | This work   | 7.15        | 5.80        | 5.85    | 0.67    |
|     | Magaña and Vázquez [51] | 6.46 | 4.42 | 5.64 | 1.02 |
|     | Experiment  | 7.69\textsuperscript{b} | 6.47\textsuperscript{b} | 4.31\textsuperscript{b} | 0.61\textsuperscript{b} |
| K   | This work   | 3.65        | 3.05        | 2.60    | 0.30    |
|     | Magaña and Vázquez [51] | 4.00 | 3.58 | 2.63 | 0.21 |
|     | Experiment  | 3.70\textsuperscript{c} | 3.20\textsuperscript{c} | 2.84\textsuperscript{c} | 0.30\textsuperscript{c} |
| Rb  | This work   | 2.60        | 2.25        | 1.80    | 0.17    |
|     | Sliwko et al [55] | 4.50 | 3.80 | 3.00 | 0.30 |
|     | Experiment  | 3.00\textsuperscript{d} | 2.40\textsuperscript{d} | 1.80\textsuperscript{d} | 0.30\textsuperscript{d} |
| Cs  | This work   | 2.15        | 1.80        | 1.40    | 0.17    |
|     | Xie et al [25] | 2.27 | 1.88 | 1.94 | 0.18 |
|     | Experiment  | 2.46\textsuperscript{e} | 2.06\textsuperscript{e} | 1.48\textsuperscript{e} | 0.20\textsuperscript{e} |

\textsuperscript{a}Felice et al [50].
\textsuperscript{b}Martinson et al [53].
\textsuperscript{c}Cowley et al [47].
\textsuperscript{d}Sliwko et al [55].
\textsuperscript{e}Kollarits et al [54].
Figure 6. Calculated elastic constants of \( C' \) and \( C_{44} \) for bcc Li (a), Na (b), K (c), Rb (d) and Cs (e) with pressure. The open squares (\( C' \)) and circles (\( C_{44} \)) are the data from [52] and [56], and the solid ones are the current theoretical results.

Figure 7. The bcc and fcc structures represented assuming a bct structure. In the fcc case, a half of the bct structure is a quarter of the fcc structure.

4. Conclusions

In conclusion, we have extensively studied the electronic properties, lattice dynamics, and elastic constants in the bcc alkali metals under pressure using the \textit{ab initio} method within the DFT. As a result of the \( s \rightarrow p \) and \( s \rightarrow d \) charge transfers, the FSs of bcc Li, K, Rb and Cs become highly anisotropic under pressure and start touching the BZ boundary at the \( N \) point at 7, 10, 5 and 1 GPa, respectively, whereas it is absent for Na. We have predicted a universal pressure-induced TA phonon softening along the \([0\xi\xi]\)-direction close to the center of the BZ.
Figure 8. The total energy variations as a function of \( c/\alpha \) for all the alkali metals at selected pressures. The curves are offset for a better view.

Table 3. The calculated elastic constants (in terms of GPa) at the predicted transition pressures of 6, 105, 15, 8 and 2.3 GPa for bcc and fcc Li, Na, K, Rb and Cs, respectively.

|       | Li  | Na  | K   | Rb  | Cs  |
|-------|-----|-----|-----|-----|-----|
| bcc   |     |     |     |     |     |
| \( C_{11} \) | 30.70 | 302.0 | 44.25 | 24.10 | 7.40 |
| \( C_{12} \) | 31.75 | 303.8 | 45.95 | 24.25 | 7.80 |
| \( C_{44} \) | 12.05 | 22.40 | 8.60  | 7.60  | 4.30 |
| \( C' \) | -0.53 | -0.90 | -0.85 | -0.08 | -0.20 |
| fcc   |     |     |     |     |     |
| \( C_{11} \) | 35.30 | 308.3 | 43.85 | 29.40 | 7.45 |
| \( C_{12} \) | 29.60 | 300.9 | 37.70 | 23.90 | 6.05 |
| \( C_{44} \) | 12.55 | 17.25 | 8.55  | 8.15  | 3.85 |
| \( C' \) | 2.85  | 3.72  | 3.07  | 2.75  | 0.70 |
| \( \Delta H^{\text{fccc}} / \text{bcc} \) (meV atom\(^{-1}\)) | -5.35 | -7.86 | -12.85 | -13.86 | -8.72 |
for all the bcc alkali metals, which is related to the instability of the $C'$ shear modulus under compression. Analysis of the calculated results suggested that the elastic instabilities associated with the softening phonon modes are the driving force of the phase transition in the bcc alkali metals. The tetragonal Bain’s paths were thus proposed for the transitions and further verified by the total energy calculation along the transition path.

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