Structure, elastic moduli and thermodynamics of sodium and potassium at ultra-high pressures

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The equations of state at room temperature as well as the energies of crystal structures up to pressures exceeding 100 GPa are calculated for Na and K. It is shown that the allowance for generalized gradient corrections (GGA) in the density functional method provides a precision description of the equation of state for Na, which can be used for the calibration of pressure scale. It is established that the close-packed structures and BCC structure are not energetically advantageous at high enough compressions. Sharply non-monotonous pressure dependences of elastic moduli for Na and K are predicted and melting temperatures at high pressures are estimated from various melting criteria. The phase diagram of K is calculated and found to be in good agreement with experiment.

64.30.+t, 64.70.Kb, 71.25.Pi

The theoretical and experimental studies of the matter properties at ultra-high pressures arouse a great interest in the connection with the possibility to obtain phases with uncommon properties as well as geophysical and astrophysical applications. As an example, the problem of metallic hydrogen can be mentioned. In the high pressure studies the alkali metals can be conveniently used as model objects. This is due, first, to their high compressibility and, second, to the variety of physical phenomena occurring in their compression and numerous structural and electron phase transitions (see, e.g., [5]). For heavy alkali metals it is the famous s–d isostructural FCC-FCC transition (see, e.g., [5], and references therein) as well as the transitions to uncommon distorted phases at higher pressures. Recently it was supposed, basing on the electron structure calculations, that lithium can transform at high enough pressures into “exotic” phases similar to that of hydrogen. Thus, further theoretical investigations of structural properties of alkali metals at ultra-high pressures seem to be interesting and important.

Despite a lot of considerations, this is still an open problem. The most of early attempts used computational approaches which were not accurate enough from the contemporary point of view. It is well known (see, e.g., [5]) that the highly accurate quantitative description of the electronic and, especially, lattice properties of metals needs the consideration of the real form of potential in the crystal and going beyond the frame of local approximation in the density functional, in particular, the allowance for generalized gradient corrections (GGA) [4]. In the present work a consistent theoretical study of the relative stability of crystal structures of Na and K under pressure as well as a variety of related lattice properties, is performed basing on these first-principle calculations. The most interesting result obtained is that, contrary to the traditional concepts (see, e.g., [1]), neither structure, which is characteristic of metals under normal conditions (BCC, FCC and HCP), is stable at high enough pressures even in Na where there are no electron transitions.

The ab initio calculations of electronic structure, thermodynamical potential, equilibrium lattice parameters and elastic moduli at temperature \( T = 0 \) were carried out using the FP-LMTO method [5] with allowance for the GGA in the form proposed in [14]. A careful optimization of the parameters of this method [5] made it possible to carry out the calculations of the total energy with an accuracy within the limits of 0.1 mRy/atom. Parameter \( c/a \) for the HCP lattice was determined by the minimization of the total energy for a fixed specific volume, and the elastic moduli — by numerical differentiation of the total energy with respect to tetragonal and trigonal deformations (see, e.g., [1]). Up to now, there are only few works devoted to the first-principle calculations of elastic moduli of metals under high pressures (see, e.g., [5] for Mo and W). The expressions for the free energy \( F \) (connected with Gibbs thermodynamical potential \( G \) by the relationship \( G = F + PV \), \( P = −dF/dV \), where \( P \) is the pressure, \( V \) is the volume) and elastic moduli \( C_{\alpha\beta\gamma\delta} \) at finite temperatures can be presented in the following form:

\[
F(V, T) = E_{el}(V) + F_{ph}(V, T)
\]

\[
C_{\alpha\beta\gamma\delta}(V, T) = C_{0\alpha\beta\gamma\delta}(V_0) + V_0 \frac{dC_{0\alpha\beta\gamma\delta}}{dV_0} P_{ph}(V_0, T) + C_{\alpha\beta\gamma\delta}^*(T)
\]

where \( F_{ph} = T \sum_{\xi, \bar{q}} \ln \left[ 2s h \omega(\bar{q}) \right] \) is the free energy of the phonon subsystem in the harmonic approximation, \( E_{el}(V) \) is the total energy of the electron subsystem obtained from the FP-LMTO calculations, \( P_{ph} = −\partial F_{ph}/\partial V \) is the phonon pressure, \( B_0 \) is the bulk modulus of the electron subsystem at \( T = 0 \), \( \xi, \bar{q}, \omega \) are the
number of phonon branch, wave vector and phonon frequency, respectively. In the expression for the elastic moduli \( C_{ij}(V, T) \) the first term corresponds to the electron contribution at \( T = 0 \), second one - to the quasiharmonic contribution due to the effects of thermal expansion, and third one - to the phonon contribution obtained from the differentiation of \( F_{ph} \) with respect to the corresponding deformation parameters. For the calculation of phonon contributions to thermodynamical functions the pseudopotential model described in [4], which describes with a high accuracy a wide range of lattice properties of alkali metals, was used.

Figs. 1,2 show the results of calculations of Gibbs potentials at \( T = 0 \) for the BCC, FCC and HCP phases of sodium and potassium, respectively. It should be noted that in the case of Na the phonon contribution to \( \Delta G \) (contribution of zero-point vibrations, \( \Delta G_{zp} \)) are \( C_{zp}^{\text{BCC}} - C_{zp}^{\text{HCP}} = 1.31 \times 10^{-5} \text{ Ry/atom} \). This is well comparable with the electron contributions to \( \Delta G \) under the normal conditions. Generally speaking, energy differences of order of \( 10^{-5} \text{ Ry/atom} \) is too small to be accurately derived in our first-principle calculations; nevertheless, we have obtained correct phase diagram even for sodium at low pressures. In accordance with the results of calculations, at \( P = 0 \) the BCC phase and HCP phase have the lowest energy for K and Na, respectively (actually, under these conditions Na has not HCP but fcc structure whose energy, however, is very close to HCP). It is important to emphasize that this difference of Na from K is purely quantitative: according to the results, shown in the insert to Fig.2, K would have to transit to the hexagonal close-packed phase at the negative pressure of the order of several kilobars. As the calculations show potassium, unlike sodium, transits from the BCC to FCC structure at \( P \approx 11.6 \text{ GPa} \), which is in excellent agreement with the experimental data [1]. In this case the relative change in the volume \( \Delta = (V_{\text{fcc}} - V_{\text{BCC}})/V_{\text{BCC}} \approx 0.0067 \) takes place at \( V_0/V = 2.14 \). Here and below \( V_0 \) is the experimental value of the specific volume at the atmospheric pressure and temperature 10K, equal to 484.12 a.u. [4]. Our calculations make it possible to suppose that the difference between Na and K is associated with the electronic topological transition occurring in the BCC potassium at \( V_0/V \approx 2 \) and destabilizing the BCC structure. The similar situation takes place in Li [1] while in the BCC sodium, within the whole range of pressures, the Van-Hove singularity goes away from the Fermi level under the compression. Generally, sodium seems to be a unique metal in the Periodical Table: in the whole region of the existence of BCC structure it has no singularities of electronic structure near the Fermi level, and the Fermi surface remains approximately spherical.

The calculation results of equations of state for sodium and potassium are shown in Fig.3 along with the experimental data available. It should be pointed out that the experimental data agree with the theoretical results within their accuracy limits (\( \approx 10\% \)). This creates the prerequisites for the development of pressure scale based on sodium as a reference substance. Note also that at room temperature the role of the phonon contribution to pressure falls under the compression, and this contribution in itself is small (of the order of 0.3 GPa at full pressure 20-30 GPa).

Figs. 4,5 display the calculation results of the dependence of elastic moduli \( C_{ij}(V) \) on the compression for sodium and potassium, respectively. A drastically non-monotonous behavior of shear moduli associated with the tetragonal \( (C'= (C_{11} - C_{12})/2) \) and trigonal \( (C_{44}) \) deformations in both BCC and FCC structures is noticeable. It should be pointed out that at least at compressions \( V_0/V < 2 \) the calculation results of \( C_{ij}(V) \) in the pseudopotential model and in the first-principle approach are close. In this region the equations of state coincide in these two approaches with an accuracy up to several percents. This confirms a sufficiently high reliability of our use of pseudopotential model for the calculation of phonon contributions to thermodynamical values. Nevertheless, the phonon contributions to the shear moduli do not exceed 10% within the whole pressure range studied. It should be noted that softening of modulus \( C' \) is a typical pre-transition phenomenon connected with the structural transitions between the BCC and close-packed structures [6]. However, the softening of modulus \( C_{44} \) in the FCC structure of K at high pressures (Fig.5) is rather surprising. It appears to be similar to the softening of this modulus, taking place in the FCC structure of Cs near the electron \( s \rightarrow d \) transition [7] and is due to the crawling of the Fermi level over the peak of \( d \)-state density.

Fig.6 shows an experimental phase diagram of potassium and the phase diagram built on the basis of our calculations. The dependence of the melting temperature on pressure, \( T_m(P) \) in the BCC and FCC phases was obtained using the phonon spectra and different melting criteria. First of all, we use the Lindeman criterion

\[
\bar{x}^2(T_m)/d^2 = \text{const},
\]

where \( \bar{x}^2(T) = \sum_{\bar{k}} \frac{n_0|\bar{q}|^2}{2M_0c_0^2} \coth \frac{h\omega_{\bar{q}}}{2T} \) is the mean square of atom displacement, \( \bar{q} \) is the polarization vector, \( M_0 \) is the atom mass, \( d \) is the distance between the nearest neighbors. Although the Lindeman criterion is empirical, it may be expected that its use for finding the melting temperature at high pressures would be as successful as at low temperatures [8]. Nevertheless one can see from Fig.6 that it is not too accurate in a broad pressure region. Varshni melting criterion [9] which is based on the temperature softening of the shear moduli, namely

\[
C_{44}(T_m)/C_{44}(0) = 0.65,
\]

appears to be much more accurate. Here we use the method of the calculation of the temperature dependence
of elastic moduli from the phonon spectra described in.
Note also that we describe with high accuracy the BCC-FCC phase boundary. We also present the results obtained in generalized Debye model when all the thermodynamical quantities are calculated in the Debye model but with the Debye temperature found from \textit{ab initio} elastic moduli. One can see that this description is also rather accurate for potassium.

Fig.1 shows that the BCC phase of sodium becomes energetically unfavorable as compared with the HCP at a pressure about 80 GPa. At $P > 100$ GPa, however, this phase demonstrates anomalies in the equilibrium value of parameter $c/a$ (Fig.7). A sharp decrease in the ratio $c/a$ to 1.2-1.3 at $V_0/V > 4.35$, which is necessary to maintain the HCP lattice in equilibrium, is doubtful actual, and seems to be indicative to transition to some non closed packed phase with a large number of atoms per cell. These phases are observed in K, Rb and Cs at high pressures. It is usual to associate their appearance in heavy alkali metals with the $s \to d$ transition. Thus, according to our results, all the three ”typically metallic” structures - BCC, FCC, HCP do not correspond to the lowest energy in Na where no electronic transitions are observed within the pressure range considered. In order to understand qualitatively the cause of appearance of ”nonstandard” metallic phases, let us use the above mentioned pseudopotential model for the estimations. In this model the radius of ”hard” ion core is described by the pseudopotential parameter $r_0$.[4] As the estimates show the compression $V_0/V \approx 4$ corresponding to the instability of the close- packed phase coincides with the condition of overlapping ion cores $2r_0 \approx d$ for Na. Hence, the concept of well determined ion cores, being at the base of standard metallic bond description, becomes inapplicable at ultra-high pressures. As a result, as we have seen, the substance transforms into exotic non close-packed phases. These results are in qualitative agreement with the results[4] for lithium.

In conclusion, note that it would be interesting to study the structure of sodium at ultra-high pressures, which, as follows from the results obtained, may prove to be surprising. Another result of this work, permitting a direct experimental check is non-monotonous behavior of Na and K shear moduli at pressure. At last, pre-
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1. S. T. Weir, A. C. Mitchell, and W. J. Nellis, Phys.Rev.Lett. \textbf{76}, 1860 (1996); R. J. Hemley and N. W. Ashcroft, Nature \textbf{380}, 671 (1996); P. P. Edwards and F. Hensel, Nature \textbf{388}, 621 (1998); W. C. Nargyara et al, Nature \textbf{393}, 46 (1998)

2. V. G. Vaks, S. P. Kravchuk, and A. V. Trefilov, Fizika Tverd. Tela \textbf{19}, 1271 (1977)

3. V.G.Vaks et al, J.Phys. F \textbf{8}, 725 (1978)

4. B.Olinger and J. W. Shaner, Science \textbf{219}, 1071 (1983)

5. K. Takemura and K. Syassen, Phys.Rev.B \textbf{28}, 1193 (1983); H.Olijnyk and W. B. Holzapfel, Phys.Lett. \textbf{99A}, 381 (1983)

6. M.Winzenick, V.Vijayakumar, and W. B. Holzapfel, Phys.Rev.B \textbf{50}, 12381 (1994)

7. C.-S. Zha and R. Boehler, Phys.Rev. B \textbf{31}, 3199 (1985)

8. H. L. Skriver, Phys.Rev. B \textbf{31}, 1909 (1985)

9. V. G. Vaks et al, J.Phys.: Cond. Matter \textbf{1}, 5319 (1989)

10. A. K. McMahan, Phys.Rev. B \textbf{29}, 5982 (1984)

11. U. Schwarz et al, Phys. Rev. Lett. \textbf{81}, 2711 (1998); Phys. Rev. Lett. \textbf{83}, 4085 (1999); Solid State Commun. \textbf{112}, 319 (1999)

12. J. B. Neaton and N. W. Ashcroft, Nature \textbf{400}, 141 (1999)

13. Y.-M. Iyan and M. Kozling, Phys. Rev. B \textbf{48}, 14944 (1993); V. Ozolins and M. Kozling, Phys. Rev. B \textbf{48}, 18304 (1993); D. L. Novikov et al, Phys. Rev. B \textbf{56}, 7206 (1997); Phys. Rev. B \textbf{59}, 4557 (1999); J. E. Jaffe, Z. Lin, and A. C. Hess, Phys. Rev. B \textbf{57}, 11834 (1997)

14. J. P. Perdew et al, Phys. Rev. B \textbf{46}, 6671 (1992)

15. S. Yu. Savrasov and D. Yu. Savrasov, Phys. Rev. B \textbf{46}, 12181 (1992)

16. N. E. Christensen, A. L. Ruoff, and C. O. Rodriguez, Phys. Rev. B \textbf{52}, 9121 (1995); K. Elinarsdotter et al, Phys. Rev. Lett. \textbf{79}, 2073 (1997); A. L. Ruoff, C. O. Rodriguez, and N. E. Christensen, Phys. Rev. B \textbf{58}, 2998 (1998)

17. S. V. Vosovskiy, M. I. Katsnelson, and A. V. Trefilov, Phys. Metal. Metallography \textbf{76}, 247 (1993)

18. R. Berliner et al, Phys. Rev. B \textbf{40}, 12086 (1989)

19. M. I. Katsnelson, I. I. Naumov, and A. V. Trefilov, Phase Transitions B \textbf{49}, 143 (1994)

20. V. G. Vaks et al, J. Phys.: Cond. Matter \textbf{3}, 1409 (1991)

21. A. M. Bratkovsky, V. G. Vaks, and A. V. Trefilov, Zh. Eksp. Teor. Fiz. \textbf{86}, 2141 (1984)

22. S. N. Vaidya, I. J. Getting, and G. C. Kennedy, J. Phys. Chem. Sol. \textbf{32}, 2545 (1971)

23. A. A. Bakanova, I. P. Dudoladov, and R. F. Truin, Fizika Tverd. Tela \textbf{7}, 1615 (1965)

24. D. Stroud and N. W. Ashcroft, Phys. Rev. B \textbf{5}, 371, (1972)

25. Y. P. Varshni, Phys. Rev. B \textbf{2}, 3952 (1970)

26. G. V. Sinko and A. L. Kutepov, Phys. Metal. Metallography \textbf{82}(2), 129 (1996)

27. N. E. Christensen, D. L. Novikov, and M. Methfessel, Solid State Commun. \textbf{110}, 615 (1999)
Figure captions

Fig.1. Pressure dependence of the differences of Gibbs potentials between BCC and FCC as well as HCP and FCC structures for Na.

Fig.2. Pressure dependence of the differences of Gibbs potentials between BCC and FCC as well as HCP and FCC structures for K.

Fig.3. Equations of states for sodium and potassium at $T = 295 \, K$. Solid line corresponds to FP-LMTO calculations, dashed line - to the calculations by the pseudopotential method. Empty (solid) triangles, circles and asterisks (squares) are the experimental data for Na and K, respectively.

Fig.4. The dependence of elastic moduli $C'$ and $C_{44}$ on the compression $U$ for BCC Na; empty circles and squares show, respectively, the data from the solid ones - the values obtained in the present work.

Fig.5. The dependence of elastic moduli $C'$ and $C_{44}$ on the compression $U$ for BCC and FCC phases of K. Solid (empty) circles and squares show $C'$ and $C_{44}$ values for BCC (FCC) phases, respectively. The dashed line — the $C'$ values for the bcc phase from the calculations.

Fig.6. Phase diagram of potassium. The solid line - experimental data, dashed line- the calculations using Varshni criterion, dashed-dot line - the calculations using Lindeman criterion, dotted line - generalized Debye model (see the text). Solid circles - BCC-FCC phase boundary from our calculations.

Fig.7. Dependence of the total energy of HCP structure for Na on the ratio $c/a$ for various compressions: the solid line — $U = 0.75$; dashed line — $U = 0.76$; dashed-dot line — $U = 0.765$. The insert shows the equilibrium values of the parameter $c/a$ for HCP structure depending on $U$ is shown. Solid (empty) circles denote the values taken in the global (local) minimum of the total energy, correspondingly.
Figure 6