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Potassium under pressure: Electronic origin of complex structures

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ABSTRACT

Recent high-pressure X-ray diffraction studies of alkali metals revealed unusual complex structures that follow the body-centred and face-centred cubic structures on compression. The structural sequence of potassium under compression to 1 Mbar is as follows:

bcc-fcc-h-g (tl19*), hP4-oP8-tl4-oC16.

We consider configurations of Brillouin-Jones zones and the Fermi surface within a nearly-freeelectron model in order to analyze the importance of these configurations for the crystal structure stability. Formation of Brillouin zone planes close to the Fermi surface is related to opening an energy gap at these planes and reduction of crystal energy. Under pressure, this mechanism becomes more important leading to appearance of complex low-symmetry structures. The stability of the *post-fcc* phases in K is attributed to the changes in the valence electron configuration under strong compression. © 2014 Published by Elsevier Masson SAS.

1. Introduction

As recent experiments show, structure and properties of material change dramatically under pressure (see review papers [1-3]and references therein). Periodic table of elements if considered in compressed state looks very different from what we are familiar with at ambient conditions. The elements on the right side of the Periodic table become close-packed metals and superconductors, like Si and Ge, whereas simple metallic structures such as bcc and fcc of the elements from the left side of the Periodic table (groups 1-2) transform under pressure to open-packed and complex structures. Na, one of the best metal in terms of conductivity and reflectivity, becomes insulating and transparent at around 2 Mbar [4]. Lithium becomes superconducting [5] below 20 K at pressures around 0.5 Mbar and at higher pressures shows a series of complex structures even with a semiconducting behaviour [6,7].

Differences between the atomic volumes of elements across one period level out under pressure (Fig. 1). This means that the elements that have the large volumes at ambient conditions have much higher compressibility. K at 112 GPa, the highest pressure reached for this element experimentally, is compressed by 6.7 times and occupies 0.15 of its initial atomic volume – the largest compression among elements achieved so far (Fig. 2). For the monovalent post-transition element Cu the value of V/V_0 at this pressure is only 0.7. Such large compression of K is accompanied by

http://dx.doi.org/10.1016/j.solidstatesciences.2014.07.008 1293-2558/© 2014 Published by Elsevier Masson SAS. the changes in electronic structure where the electronic levels overlap. Some suggestions of the mechanism have been made, however they don't explain all the observations and questions remain. Interestingly, similar complex structural arrangements are observed for the elements from the right side of the periodic table (groups 13–16), with atomic volumes close to the values measured for the group 1 and 2 elements (Fig. 1).

Argon is the closed-shell element next to potassium in the Periodic table. Experimental P-V data for argon [12] are also shown in Fig. 2. At 20 GPa the atomic volume of K (fcc, around the II–III transition) is ~45% *larger* than that of Ar, and above ~60 GPa the atomic volume of K becomes *smaller* than that of Ar, and on further compression to 112 GPa is ~7% smaller (in the K-oC16 phase). Volume changes with pressure for K are compared with P–V data for Ge to underline the similarity of their atomic volumes at pressure of ~100 GPa when they both adopt the same crystal structure *o*C16 where the compression of Ge is $V/V_0 \sim 0.5$ [13,14]. These volume changes in compressed K imply significant changes in electronic structure.

Potassium belongs to the group-I elements — alkali metals — lying in the intermediate position between light (Li, Na) and heavy (Rb, Cs) alkalis. At ambient condition all alkali elements crystallize in the body-centred cubic structure (bcc) and are considered as free-electron metals. The first observed transformation on compression for all alkalis was to face-centred cubic structure (fcc) and further transitions were to complex structures summarized in Table 1. In addition to phases in Table 1, several very complex structures were observed for sodium at pressures above 100 GPa in





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Fig. 1. Atomic volumes of the elements as a function of the group number for the elements in the IV period of the Periodic table. Open symbols correspond to the volume at ambient conditions. Filled symbols correspond to the pressure of 100 GPa (1 Mbar) and are taken from the experimental measurements done by authors and found in the literature (see review papers [1-3] and references therein).

the vicinity of the minimum of the melting curve determined as *t1*50, *o*C120, *mP*512, *aP*90 [15].

Potassium in its structural sequence under pressure comprises features of the structural sequences of the lighter element Na as well of the heavier elements Rb and Cs. K has however its own special features as for example the absence of a distortive bcc structure *cl*16 observed in the light alkalis Li and Na or related complex structures *oC*52 in Rb and *oC*84 in Cs. These intermediate *post*-fcc structures are missing in K and fcc was observed to transform into a host-guest (*tl*19^{*}) structure or into a hexagonal *hP*4 structure.

Peculiarities in structural behaviour of K under pressure are based on specific features of its electron configuration: K opens in the Periodic table the first long period with 3d transition metals. The empty 3d electron band in K is just above the valence electron 4s level and under pressure there is s - d transition [16]. In heavy alkalis Rb and Cs that have d-levels in their cores electron transitions start at lower pressures than in K. In lighter element Na the 3d



Fig. 2. Atomic volumes of potassium on compression in comparison with Ar, Ge and Cu (K: [8–10], Cu: [11], Ar: [12], Ge: [13,14]). Relative compression of K and Cu is shown in the insert.

level is well above the 3s valence electron level therefore fcc in Na is stable up to a very high pressure of ~100 GPa.

As was considered in Ref. [16] the electron configuration of an element essentially changes under strong compression due to broadening and overlapping of electron levels and as a result of these changes an electron transfer may occur from core levels into the valence band (i.e. core ionization). Structural transformations of alkali metals from close-packed structures to open-packed and low-coordinated structures indicate convincingly that valence electron configuration is changed. In our recent paper on sodium [17] the question has been raised whether the core ionization takes place for Na in the *oP8* structure where compression is V/V_0 ~0.25 and a transition to the divalent state was proposed.

In this paper we investigate possible causes that contribute to the formation of the complex crystal structures in elements under pressure, which have similar crystal structures and atomic volumes for the elements from the left and from the right of the Periodic table. We look at the phase transition sequence of K in details and offer a comparison to other similar structures observed in elements and compounds, as well as suggest the electronic cause for the formation of its crystal structures.

2. Method of analysis

The stability of high-pressure phases in potassium are analyzed within a nearly free-electron model with the Fermi sphere radius defined as $k_F = (3\pi^2 2z/V)^{1/3}$, where *z* is the number of valence electrons per atom and *V* is the atomic volume. The energy of valence electrons is decreased due to a formation of Brillouin planes with a wave vector q near the Fermi level k_F and opening of the energy pseudogap on these planes if $q_{hkl} \approx 2k_F$. This effect, known as the Hume-Rothery mechanism, was applied to account for the formation and stability of the intermetallic phases in binary simple metal systems like Cu–Zn [18–21], and then extended to explain the stability of complex phases in various systems, from elemental metals [2,22] to intermetallics, quasicrystals and their approximants [23,24].

A computer program BRIZ [25] has been recently developed to construct Brillouin zones or extended Brillouin-Jones zones (BZ) and to inscribe a Fermi sphere (FS) with the free-electron radius k_F . The resulting BZ polyhedron consists of numerous planes with relatively strong diffraction factor and accommodates well the FS. The volume of BZ's and Fermi spheres can be calculated within this program. The BZ filling by the electron states (V_{FS}/V_{BZ}) is estimated by the program, which is important for the understanding of electronic properties and stability of the given phase. For a classical Hume-Rothery phase Cu₅Zn₈, the BZ filling by the runary other phases stabilized by the Hume-Rothery mechanism.

Diffraction patterns of these phases have a group of strong reflections with their q_{hkl} lying near $2k_F$ and the BZ planes corresponding to these q_{hkl} form a polyhedron that is very close to the FS. Input data are lattice parameters, number of atoms in the unit cell and average number of valence electrons per atom. Output data allow for estimation $V_{\rm ES}/V_{\rm BZ}$ and comparison of $q_{\rm hkl}$ with $2k_{\rm F}$. The FS would intersect the BZ planes if its radius, k_{F} is slightly larger then $q_{\rm hkl}/2$, and the program BRIZ can visualize this intersection. One should keep in mind that in reality the FS would usually be deformed due to the BZ-FS interaction and partially involved inside the BZ. The ratio $2k_F/q_{hkl}$, called a "truncation" factor or a "closeness" factor [26], is an important characteristic for the FS-BZ approximation. For Hume-Rothery phases such as Cu₅Zn₈, this closeness factor is equal 1.015, and it can reach up to 1.05 in some other phases. This means that the FS radius can be up to approximately 5% larger than the BZ vector $q_{\rm hkl}/2$ for the phase to be Download English Version:

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