Structural phase transition of potassium under high-pressure and low-temperature condition

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Abstract. We performed electrical resistance and powder X-ray diffraction measurements of potassium under high-pressure and low-temperature condition. In the temperature dependence of resistance under several pressure, no superconducting transition was observed below 1 K. From the powder X-ray diffraction measurement, the K-III phase, it has a host-guest structure, is stable in wide pressure range. Furthermore, the K-IV phase disappeared and the amorphous-like region with no X-ray diffraction peaks appeared at low temperature below 150 K.

1. Introduction
Superconductivity in elements under high pressure has been investigated intensively. At present, 53 elements have been reported as the superconductor at low temperature. Especially, 23 of superconducting elements shows the superconductivity only under high pressure. Among superconductive elements, relatively high superconducting transition temperature ($T_c$) of around 20 K has been observed in light alkali and alkali earth metals, lithium and calcium [1,2]. The alkali and alkali earth metals show the successive pressure-induced structural phase transitions. The phase transition causes to the drastic change of electronic properties of elements under high pressure. For example, the lithium indicates the re-entrant metal-insulator-metal transition related to the borders between each structural phases. In the case of the calcium, superconductivity emerges in the Ca-III phase and the $T_c$ rising tendency is observed below Ca-VII phase. It is noted that the $T_c$ shows the maximum in the Ca-VII which has a host-guest structure [3]. The host-guest structure is commonly appeared under high pressure among alkali earth metal elements (calcium, strontium, and barium) and the maximum of $T_c$ is in the high pressure phase with this structure.

Among alkaline metal elements, lithium and cesium show superconductivity under high pressure. On the other hand, other alkaline metals reported no superconductivity yet. At room temperature, potassium shows successive pressure-induced structural phase transition as body-centered cubic (bcc) $\rightarrow$ face-centered cubic (fcc, 12 GPa) $\rightarrow$ K-III (22 GPa) $\rightarrow$ K-VI ($\alpha$P8, 54 GPa) $\rightarrow$ K-V (90 GPa) [4]. K-III phase is a host-guest structural phase similar to Ca-VII phase showing relatively high-$T_c$ superconductivity under high pressure. Therefore, K-III phase has a possibility of superconductivity under high pressure. However, the no superconducting transition is reported in the $T$-$P$ region below 1.5 K up to 17 GPa and below 4 K up to 44 GPa [5]. In contrast to experimental absence of
superconductivity on potassium even if under high pressure, several theoretical calculation suggests that the possibility of superconductivity on potassium. For example, Profeta et al. calculated that the $T_c$ in fcc phase is estimated about 3 K and with increasing pressure, $T_c$ rise to about 10 K in K-III phase from a first principle investigation [6].

The investigation of phase transition at low temperature is important to understand the ground state such as superconducting state because of difference structure between room and low temperatures. For example, it is reported that the simple cubic structure of Ca-III phase is distorted at low temperature by several research groups including us [2, 7]. Additionally, tetragonal Ca phase with $I4_1/amd$ structure is observed only at low temperature below 10 K under the pressure at 30–40 GPa, which is close to the border between Ca-II (fcc) and Ca-III (sc) phases [8]. The superconductivity of calcium is observed as a small resistance drop at 2 K and 44 GPa [9], this pressure is just above the $I4_1/amd$ phase of calcium.

In this study, we investigate about pressure-induced structural phase transition at low temperature and superconductivity of potassium from electrical resistance and powder X-ray diffraction measurements using diamond anvil cell (DAC).

2. Experimental
A potassium block with a stated purity of 99.95 % was purchased from Aldrich Chemical Company. The sample settings to a DAC for electrical resistance and powder X-ray diffraction measurements were performed in an argon atmosphere to prevent sample oxidization or any other chemical reaction. No pressure medium was used. For the electrical resistance measurement, the copper film deposited on the diamond culet was used as an electrode with 4-probe arrangement. Aluminum oxide was used as an insulating layer on a rhenium metal gasket. The ac-resistance of potassium sample in the DAC was measured by using the ac resistance bridge LR-700 (Linear Research Inc.). The pressure was determined by using ruby fluorescence method. The X-ray diffraction experiments were carried out by an angle-dispersive method using an image-plate detector. High-quality X-ray diffraction patterns of potassium under high-pressure and low-temperature condition were obtained by the synchrotron radiation BL10XU in SPring-8. In the case of the X-ray diffraction measurement, the pressure determined by using the frequency shift of diamond Raman peak by pressurization.

![Figure 1. Temperature dependence of electrical resistance under pressure at 13 and 19 GPa.](image)

3. Results and discussions
3.1. Temperature dependence of resistance under high pressure.
Figure 1 shows the temperature dependence of resistance of potassium under several pressures as 13 and 19 GPa in fcc phase. In this phase, metallic temperature dependence of resistance and no superconducting transition was observed below 1 K. It coincides with previous report about no superconductivity in fcc phase. Additionally, the partially insulating behaviour appeared from 80 to 70 K. The pressure was determined only at room temperature and the DAC has a possibility of pressure changing during a cooling-heating cycle. One of possible reason of the anomaly in resistance around
70 K is a crossing the boundary between fcc and K-III phase at low temperature because the pressure at 19 GPa is close to the boundary (22 GPa). Other is any electronic transition such as a charge density wave (CDW). In order to reveal the reason of this anomaly, the pressure dependence of anomaly such as a shift of characteristic temperature is important. However, the diamond anvil was broken and there is no result about pressure dependence of resistance just above 19 GPa. At present, there are no more information about this anomaly.

3.2. Phase diagram from the powder X-ray diffraction measurement under high pressure.
Figure 2(a) shows several powder X-ray diffraction patterns under some high-pressure and low-temperature conditions. At around 30 K, the potassium sample shows pressure-induced structural phase transitions to fcc and then K-III phases under similar pressure to that at room temperature. Therefore, phase boundaries between bcc and fcc, fcc and K-III phases are almost temperature-independent. On the other hand, the transition from K-III phase was observed above 80 GPa at low temperature. Furthermore, the K-IV phase disappeared at low temperature and no X-ray diffraction peaks observed above about 100 GPa, it is amorphous-like behavior. With increasing pressure, the X-ray diffraction peaks re-appeared above about 130 GPa by phase transition to higher-pressure phase.

Figure 2(b) shows the $P$-$T$ phase diagram determined from powder X-ray diffraction. The arrows indicate the pressure-temperature pathway during measurements. The pressure region of K-III phase with host-guest structure at low temperature is extended to higher pressure than at room temperature. At present, the superconductivity has been researched only up to 44 GPa. The extension of pressure region of K-III phase suggests the possibility of superconducting phase above 44 GPa. The K-IV phase is observed only above 150 K and amorphous-like region without long-range structural ordering appears at low temperature. It possibly indicates that several crystal structures have similar stability and thermal energy is needed to the structural transition from K-III to higher-pressure structural phase. Under higher pressure than amorphous-like region, structural high-pressure phase appeared. In this study, we could not determine the crystal structure of this high pressure phase at low temperature because of hinderance by large peaks from Re gasket. It seems that the diffraction pattern of this high pressure phase is inconsistent with reported pattern of K-V phase at room temperature [4]. However, reported structural analysis determines the crystal structure of K-V phase as a mixture of two different structures ($tI4$ and $oC16$) [4]. Therefore, it is difficult to compare with our measured pattern.
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