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Observation of the *oP*8 crystal structure in potassium at high pressure

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Ab initio electronic structure calculations on potassium at high pressure reveal that the orthorhombic *oP*8 structure, found recently in sodium, has a lower enthalpy in potassium than do other candidate crystal structures recently reported to be stable at high pressure [Y. Ma, A. R. Oganov, and Y. Xie, Phys. Rev. B **78**, 014102 (2008)]. Subsequent powder-diffraction studies to above 100 GPa confirm *oP*8 to be the stable phase of potassium from 54(2) to 90(2) GPa, where it transforms to the tetragonal *tI*4 structure, which in turn transforms to the orthorhombic *oC*16 structure at 96(3) GPa.

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At ambient conditions, the single valence electrons in the alkali metals (Li, Na, K, Rb, and Cs) have only very weak interactions with the ionic cores, and these metals are therefore regarded as "simple," with electronic properties that are well described by the nearly-free electron (NFE) model. The behavior of such metals at high pressure, where the NFE model is no longer valid, is of fundamental interest. In the last decade, a large number of computational, structural, and physical property studies have revealed a wealth of unexpectedly complex behavior in Li,[1–6] Na,[7–11] Rb,[12–14] and Cs.[15–17] In contrast, over the same period, K has received relatively little attention and, for example, its structural behavior is only reported to ~30 GPa,[18] significantly lower than for any other alkali metal. However, a recent computational study of Li, K, Rb, and Cs, using an evolutionary algorithm to search for the lowest-energy structures, predicted that the phase transition sequence in K above 25 GPa would mirror that known in Rb and Cs.[19] Specifically, it was predicted that the tetragonal *tI*4 structure (*tI*4 is a standard notation[20] designating the lattice symmetry and the number of atoms in the unit cell) found in Rb-V (Ref. 21) and Cs-IV (Ref. 22) would be stable in K at 40 GPa and that this would transform to the orthorhombic *oC*16 structure [found in Rb-VI (Ref. 23) and Cs-V (Ref. 16)] at 80 GPa. The transition pressures between the same two phases in Rb and Cs are 48.5 and 10 GPa, respectively.[24] Ma *et al.*[19] noted, however, that the incommensurate nature of K-III, the stable crystal structure of K at 23 GPa,[18] precluded them from including this phase in their enthalpy calculations. The transition pressure from the incommensurate phase to the *tI*4 structure was therefore not calculable.

Since the computational work of Ma *et al.*,[19] we have reported a detailed diffraction study of the high-pressure phase-transition sequence in Na above 100 GPa. We have found that an orthorhombic structure with space group *Pnma* and eight atoms per unit cell (*oP*8-Na) is the stable phase between 117 and 125 GPa at room temperature,[10] with an incommensurate phase stable above 125 GPa.[11] Although Ma *et al.*[19] searched for candidate structures with 4, 6, 8, 12, and 16 atoms per unit cell in their predictions for the high-pressure behavior of K, they did not report finding the *oP*8 structure as a low-energy candidate. It would be interesting if the *oP*8 phase were stable in K because that would indicate high-pressure behavior more like that of its lower-*Z* neighbor Na than its higher-*Z* neighbors Rb and Cs. In Na, the unusual high-pressure behavior is suggested to arise from the mixed *p*-*d* character of the orbitals, whereas in Rb and Cs the behavior is dominated by the *d* electrons arising from pressure-induced *s*-*d* charge transfer.[19]

To investigate whether the *oP*8 structure is indeed an equilibrium high-pressure phase of K, we have first made calculations of the enthalpies of the *oP*8, *tI*4, and *oC*16 phases over the pressure range of 25–100 GPa. We find that the *oP*8 structure does indeed have a lower enthalpy than the *tI*4 structure over part of that range, making it at least possible that it is an equilibrium high-pressure phase. Subsequent high-pressure powder-diffraction studies at the Diamond Light Source have confirmed *oP*8 as an equilibrium high-pressure phase between 54 and 90 GPa at room temperature. Full Rietveld refinement of the structure at 58(1) GPa shows it to be in excellent agreement with that obtained in our computational study and slightly different from *oP*8-Na.[10]

Electronic structure calculations were carried out within the density-functional theory (DFT) formalism with a plane-wave pseudopotential approach, as implemented in the Vienna *ab initio* simulation package.[25] We used the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) for the exchange-correlation functional[26] and the projector augmented wave (PAW) all-electron description of the electron-ion-core interaction.[27] To avoid core overlap at high compressions, we treated the 3*s*, 3*p*, and 4*s* states for potassium as valence electrons, as was also done by Ma *et al.*[19] Brillouin-zone integrals were approximated using the method of Monkhorst and Pack,[28] and the energies converged with respect to *k*-point density ($13\times15\times9$, $16\times16\times10$, and $12\times12\times12$ *k* meshes for the *oP*8, *tI*4, and *oC*16 structures, respectively) and to the plane-wave cutoff (390 eV). All structural relaxations were performed via a conjugate-gradient minimization of the total energy using the Methfessel-Paxton method.[29] For the final calculation of the optimized crystal structures the tetrahedron method with Blöchl corrections was used.[30] $G(P)$ curves are calculated within the static approximation (zero temperature and neglecting zero point vibrational contributions).

The calculated enthalpy differences H-H_{fcc} (kcal/mol) versus pressure for the *oP*8, *tI*4, and *oC*16 structures of K relative to the lower-pressure face-centered cubic (fcc) phase

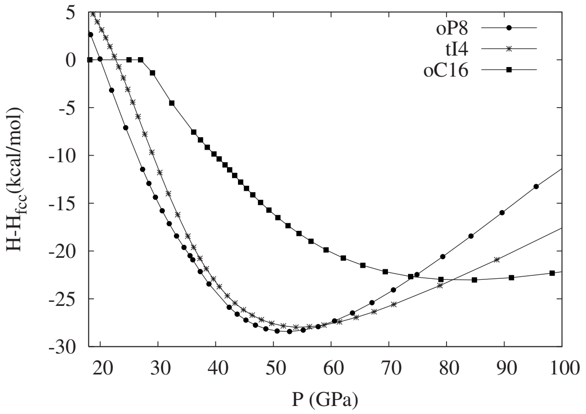

FIG. 1. Enthalpy differences, relative to the low-pressure fcc structure, as a function of pressure for the *oP*8, *tI*4, and *oC*16 structures in K. The calculations show that the *oP*8 phase is the most energetically favorable of the three at pressures of up to 58 GPa, where it transforms to *tI*4, which in turn transforms to the *oC*16 structure at 81 GPa.

are shown in Fig. 1. The results show that the *oP*8 structure becomes more energetically favorable than fcc at 20 GPa and has a lower enthalpy than the *tI*4 structure until 58 GPa. The incommensurate nature of K-III prevents us from determining its enthalpy, but we expect it to have the lowest enthalpy over the pressure range where it is the experimentally observed equilibrium phase, which we show in this study to extend to 54 GPa. That phase aside, our calculations clearly show that, rather than the predicted *tI*4 structure at 40 GPa,[19] the most favorable structure at pressures up to 58 GPa is the orthorhombic *oP*8 structure previously observed in Na.[10] Above that pressure, our calculations suggest that the enthalpy of the *oP*8 phase becomes unfavorable with respect to the *tI*4 phase, which in turn transforms to the *oC*16 phase at a pressure of 81 GPa, in excellent agreement with the value predicted for this transition by Ma *et al.*[19] The electronic band structure of *oP*8-K at 58 GPa shows it to be a semimetal with an indirect Σ-Y band overlap of 1.2 eV and a low density of states (DOS) and a pseudogap near the Fermi level.

Experiments to test for the existence of the *oP*8 phase were conducted on commercially purchased samples of K with a stated purity of 99.99%. Diamond-anvil cells equipped with tungsten gaskets were loaded in a dry oxygen-free atmosphere in a glovebox in order to avoid contamination, and no pressure transmitting medium was used. The pressure was determined by the ruby fluorescence method using a small piece of ruby enclosed with the sample.[31] Powder-diffraction data were collected at room temperature on beamline I15 at the Diamond Light Source using a wavelength of 0.4403 Å. A diffraction profile at 112 GPa was also collected at the European Synchrotron Radiation Facility using a wavelength of 0.4142 Å. The two-dimensional (2D) diffraction images were integrated azimuthally,[32] and structural information was obtained by least-squares fitting to measured peak positions and by Rietveld refinement of the integrated diffraction profiles.[33]

Diffraction patterns of the low-pressure body-centered cubic (bcc) and fcc phases of K showed no discernible contaminant peaks, confirming that the samples were pure potassium. Upon pressure increase, the transition to the incommensurate K-III phase was observed at 20 GPa, in agreement with our previous study.[18] Further compression showed that K remained as a host-guest composite structure to 54 GPa and confirmed the changes in the ordering of the guest chain atoms reported previously at 31 GPa.[18] Full details of the complex behavior of the composite structure will be reported separately.

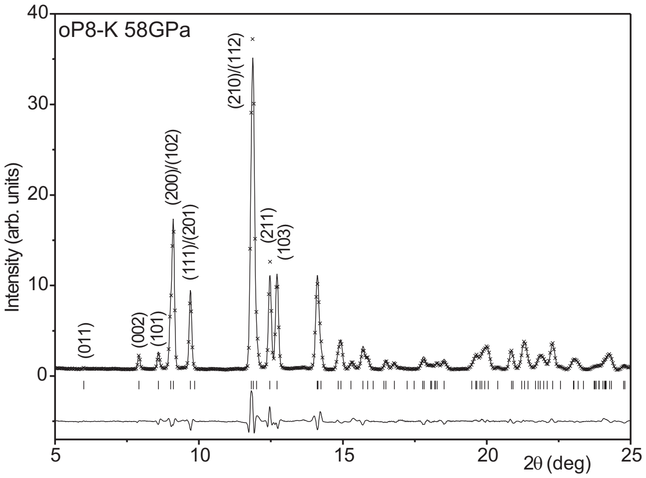

FIG. 2. Rietveld refinement of the *oP*8-K diffraction profile at 58(1) GPa. Tick marks below the profile show calculated peak positions, and the difference between observed (crosses) and calculated (line) profiles is shown under the tick marks. Some low-angle reflections are indexed.

At 54(2) GPa, new peaks began to appear in the diffraction patterns, accompanied by the disappearance of the peaks from the host-guest phase. The transition was complete at 56 GPa, and the diffraction pattern at 58(1) GPa is shown in Fig. 2. Comparison of the observed diffraction pattern with that calculated from the predicted *tI*4 structure at this pressure[19] shows them to be quite different. However, the calculated diffraction pattern from the *oP*8 phase predicted by our calculations is very similar to what we observe. Using the calculated *oP*8 structure as a starting model, Rietveld refinement of the 58 GPa diffraction profile, including a correction for preferred orientation, proceeded straightforwardly to give the excellent fit shown in Fig. 2.

The *oP*8 phase of potassium is stable to 90(2) GPa, where the appearance of a new diffraction peak marks a structural phase transition (see inset to Fig. 3). This feature becomes more intense upon pressure increase to 100 GPa, where the appearance of further new diffraction peaks mark a second structural transition at 96(3) GPa (see inset to Fig. 3). Further pressure increase to 107 GPa resulted in a mixed-phase profile of the new peaks and only a trace still remaining of the *oP*8 phase. The presence of intense diffraction peaks from the gasket initially prevented a definitive interpretation of the new peaks. However, a diffraction image collected at 112 GPa at the ESRF, using a considerably smaller x-ray beam (Fig. 3), was readily fitted as a mixture of the *tI*4 structure of Rb-V and Cs-IV and the *oC*16 structure of Rb-VI and Cs-V, respectively. This showed the peak at 13° (2θ) to be solely

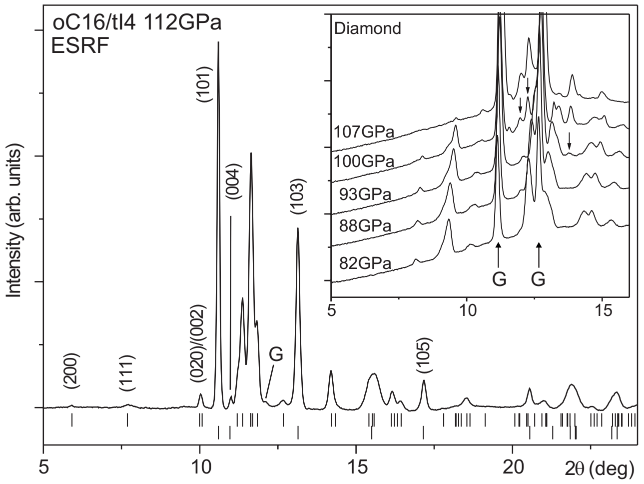

FIG. 3. The inset shows the low-angle region of a series of diffraction profiles collected on pressure increase from 82 to 107 GPa at DLS. New diffraction peaks first seen in the profiles at 93 and 100 GPa (highlighted with arrows) mark the appearance of new phases. The main figure shows the mixed-phase *tI*4/*oC*16 diffraction profile obtained at 112 GPa at the ESRF. Tick marks below the profile show the calculated peak positions of the (lower) *tI*4 and (upper) *oC*16 phases. Some low-angle reflections are indexed, and peaks marked with a G come from the Re gasket.

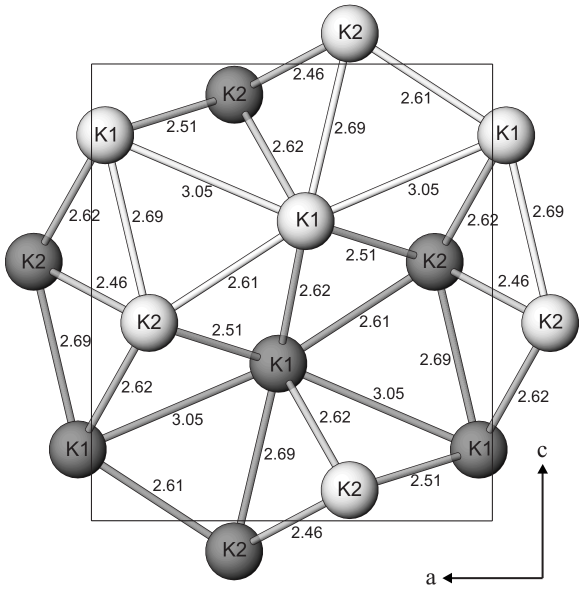

FIG. 4. (a) Crystal structure of *oP*8-K at 58 GPa as viewed down the crystallographic *b* axis. Light gray atoms are at $y=\frac{3}{4}$, and dark gray atoms are at $y=\frac{1}{4}$. K1 and K2 atoms are located at $(x_1,\frac{1}{4},z_1)$ and $(x_2,\frac{1}{4},z_2)$, respectively; see Table I. Bonds are shown between both nearest-neighbor atoms and next-nearest neighbors, and interatomic distances are given in Å beside each bond.

the (103) reflection of *tI*4, and hence we can conclude that it is this phase that appears at the 90(2) GPa transition. The refined lattice parameters of the *tI*4 and *oC*16 structures obtained from the 112 GPa mixed-phase profile are $a=2.322(1)$ Å, $c=8.669(1)$ Å, and $a=8.032(1)$ Å, $b=4.753(1)$ Å, and $c=4.716(1)$ Å, respectively. From extrapolation of the *tI*4 and *oC*16 lattice parameters obtained at 100, 107, and 112 GPa, the volume changes $(\Delta V/V_{\text{trans}})$ at the *oP*8→*tI*4 and *tI*4→*oC*16 transitions at 90(2) and 96(3) GPa are 0.2(4)% and 3.7(4)%, respectively. An *oP*8→*tI*4 transition is not known in any of the other alkali metals. The volume changes at the *tI*4→*oC*16 transition in Rb and Cs are 3.3% and 9.3%, respectively.[16,21]

The refined structural coordinates from the Rietveld refinement of *oP*8-K at 58(1) GPa are given in Table I, along with those calculated for *oP*8-K at the same pressure and those determined previously for *oP*8-Na at 119(2) GPa. The agreement between observed and calculated *oP*8-K structures is excellent: the lattice parameters agree to within 2%, while the observed and calculated atomic coordinates are almost identical. The *oP*8-K structure is slightly different from that observed in *oP*8-Na, in particular in the lattice parameter ratios. The refined *oP*8 structure of K at 58(1) GPa, as viewed perpendicular to the *ac* plane, is shown in Fig. 4. The structure comprises *ac* planes of atoms with fractional coordinates along the *b* axis of $y=\frac{1}{4}$ or $\frac{3}{4}$, but the structure itself is not layered, and the shortest interatomic distance of 2.46 Å at 58 GPa is between two K2 atoms with different *y* values. Each K1 atom has two nearest neighbors at 2.61 and 2.69 Å within the same *ac* plane and a further six at distances of 2.51 and 2.62 Å in the planes above and below. In addition, there are two K1 next-nearest-neighbor atoms within the same *ac* plane at 3.05 Å. The resulting coordination of the K1 atoms is thus 8+2. The K2 atoms also have eight nearest neighbors, two within the same *ac* plane and six in the planes above and below. However, they have no next-nearest neighbors at ~3 Å.

The observation of the *oP*8 structure in K reveals it to have a pressure-induced structural behavior like that of Na, as well as having behavior like Rb and Cs as indicated by the observation of the *tI*4 and *oC*16 phases. The similarity to Na is unexpected in relation to the recent electronic structure calculations of Ma *et al.*[19] As noted, they found K, Rb, and

TABLE I. Calculated lattice parameters, volume per atom, and fractional atomic coordinates of *oP*8-K at 58 GPa in space group *Pnma*; the refined structure of *oP*8-K at the same pressure; and the refined structure *oP*8-Na at 119(2) GPa (Ref. 10). The K1 and K2 atoms occupy two fourfold 4*c* sites at $(x_1,\frac{1}{4},z_1)$ and $(x_2,\frac{1}{4},z_2)$, respectively.

	P (GPa)	*a* (Å)	*b* (Å)	*c* (Å)	V_{atom} (Å^3)	x_1	z_1	x_2	z_2
*oP*8-K (calc)	58	5.705	3.266	6.377	14.85	0.033	0.156	0.143	0.568
*oP*8-K (obs)	58(1)	5.602(1)	3.311(1)	6.380(1)	14.792(6)	0.034(1)	0.156(1)	0.144(1)	0.567(1)
*oP*8-Na (obs)	119(2)	4.7650(5)	3.020(3)	5.251(2)	9.45(1)	0.015(1)	0.180(1)	0.164(1)	0.586(1)

Cs to have the same high-pressure structural sequence, and they attributed this to these heavier alkalis' being dominated by *d* electrons arising from *s*-*d* transfer, whereas the ultrahigh pressure behavior of Na arises, they suggest, from *p*-*d* hybridization. Thus our results question this picture of a simple dependence of structural stability on *d*-electron dominance or *p*-*d* hybridization.

It is interesting to understand why the evolutionary algorithm used by Ma *et al.*[19] failed to find the *oP*8 phase as a low-energy candidate. The most likely explanation is that the relatively small calculated enthalpy difference between the *oP*8 and *tI*4 phases (see Fig. 1) is coupled with a high kinetic barrier. But, given the similarity of our methods and the very close agreement between our calculated value for the *tI*4 to *oC*16 transition and that obtained by Ma *et al.*,[19] it seems likely that had they found *oP*8, Ma *et al.*[19] would have calculated the same relative enthalpy and transition pressure to *tI*4 as we do.

The fact that our calculations predict an *oP*8 to *tI*4 transition at 58 GPa (Fig. 1) raises the question as to why the *tI*4 phase, predicted to be stable between 58 and 81 GPa, is found experimentally from only 90 to 96 GPa. These differences are too large to be attributed to plausible hysteresis in the experiments. Some discrepancy may arise since the calculations are performed at 0 K where all entropic contributions to phase stability are neglected while the experiments are at room temperature, but again the effect is too large to be completely due to this. Another possible factor is that the GGA exchange functional may not describe energy differences well if the type of bonding is very different between *oP*8 and *tI*4, especially if the *oP*8 phase is associated with stronger electron correlation, as its much lower metallicity might suggest and as has been reported in *oP*8-Na.[34]

In conclusion, *ab initio* calculations show that the orthorhombic *oP*8 structure, found previously only in Na, is a stable high-pressure phase of K, and powder-diffraction studies confirm *oP*8 to be stable from 54(2) to 90(2) GPa. The results thus show that K differs from the high-pressure behavior of Rb and Cs in sharing an *oP*8 phase with Na, even though K has the possibility of 4*s*-3*d* hybridization of electron states, as found in Rb and Cs, rather than the *p*-*d* hybrid character of Na. This suggests that some aspects of electronic structure other than the atomic orbital picture must play a role in structural stability.

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