High-pressure x-ray diffraction on potassium and rubidium up to 50 GPa

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The effect of pressure on structural properties of potassium and rubidium is studied with diamond-anvil cells by energy-dispersive x-ray diffraction with synchrotron radiation at room temperature up to 50 GPa. The K III structure of potassium at pressures above 23 GPa is indexed by the use of a tetragonal-body-centered lattice (tI16) with 16 atoms in the unit cell. A new phase is found for rubidium above 46 GPa. Equation of state data for these heavy alkali metals are presented and compared with earlier data for cesium.

INTRODUCTION

The alkali metals are of special interest in high-pressure physics, particularly because of their apparently simple electronic structure with just one conduction electron outside the closed-shell configurations, which makes them specially interesting for comparison with different theoretical models. At ambient conditions all the alkali metals crystallize in the cubic-body-centered *cI*2 structure type. Pearson symbols are used throughout this paper as recommended by IUPAP.[1] Under pressure a wide variety of more or less complex phases has been observed and reviewed[2] in recent years. The heavy alkali metals potassium, rubidium, and cesium show, under pressure, first a phase transition from *cI*2 to *cF*4. The transformation pressures are 11.6 GPa, 7 GPa, and 2.25 GPa, respectively.[3–6] In connection with these phase transitions, the occupation of the *d* valence band plays an important role. Band-structure calculations for these elements show a rising of the *d*-band occupation under pressure.[7–9] This phenomenon is known as $s \rightarrow d$ transfer, and drives the bcc→fcc transition.[2]

At higher pressure all heavy alkali metals transform into more complex structures; thereby Rb V and Cs IV have been identified as the same *tI*4 structure,[3,10] whereas the structures of K III, as well as for Rb III, IV, and VI have not been solved.[11] Thus the improvements in diamond anvil cell (DAC) techniques and energy dispersive x-ray diffraction (EDXD) with synchrotron radiation stimulated the present attempt to solve the open questions.

EXPERIMENTAL DETAILS

Potassium and rubidium were studied by energy dispersive x-ray diffraction up to 50 GPa at HASYLAB with synchrotron radiation. The technical details have been given previously.[12]

The experiments were performed with different DAC's at room temperature, using the ruby luminescence technique with the nonlinear pressure scale[13] for pressure determination from the shift of the ruby R_1 fluorescence line. The samples were embedded in inconel gaskets with oil as the pressure transmitting medium. During the preparation the highly reactive samples were always protected by mineral oil (white) against oxidation. Recording times for the diffraction pattern were typically 1 h.

STRUCTURAL RESULTS

Potassium. Figure 1 shows a typical x-ray-diffraction pattern for the complex phase K III taken in the course of increasing pressure. K III is observable above 23 GPa, and no further phase transition has been noticed up to the present maximum pressure of 51.4 GPa. In this pres-

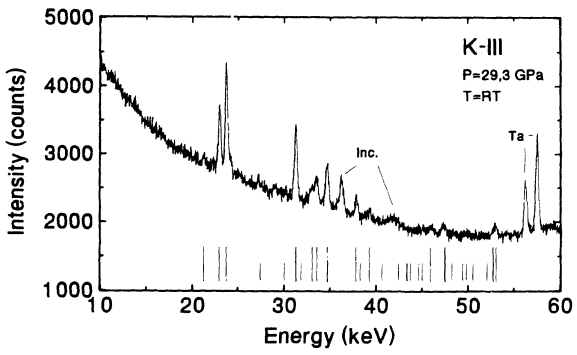

FIG. 1. EDXD spectrum for K III at 29.3 GPa and ambient temperature. The calculated positions of the diffraction lines for a *tI*16 structure are shown by vertical bars below the measured data. Longer lines represent observed and short lines unobserved peaks. Heavier lines indicate overlapping lines. "*Inc.*" and "*Ta*" mark the diffraction lines of the gasket material and the fluorescence lines of tantalum caused by the used slit system.

TABLE I. Comparison of experimental and calculated d spacings for K III at 29.3 GPa with indexing for the $tI16$ structure type. The diffraction lines marked with stars were observed in other patterns. Diffraction lines, which could not be observed separately with the technique used are connected by straight lines.

d (obs.)/pm	d (calc.)/pm	Diff./pm	hkl
336.8	337.0	0.19	220
311.5	311.8	0.28	211
301.6	301.4	−0.20	310
	260.9*		301
	238.3*		400
228.8	228.9	0.07	321
	228.6	−0.23	002
	224.7		330
216.6	216.4	−0.17	112
213.3	213.1	−0.12	420
206.3	206.3	−0.01	411
	206.1	−0.23	202
188.9	189.2	0.23	222
	186.9		510
182.1	182.1	0.03	312
	175.9		431,501
	168.5		440
	165.1		521
	164.9		402
	163.5		530
	160.2		332
	158.9		600
155.7	155.9	0.30	422
151.0	150.7	−0.29	620
	150.5	−0.55	103
	148.2		611
	144.7		512
	143.5		213
	141.5		541
	137.4		303
	135.7	0.55	631
135.1	135.6	0.49	442
	134.8	−0.33	550,710

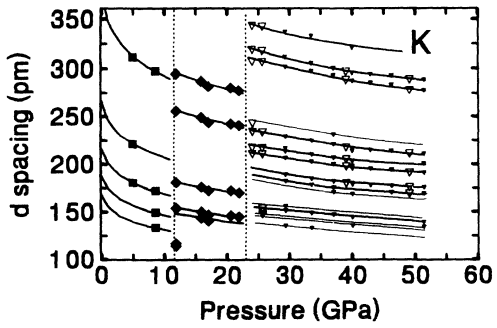

FIG. 2. Pressure dependence of d spacings for K. The solid and open symbols represent points taken on increasing and decreasing pressure, respectively.

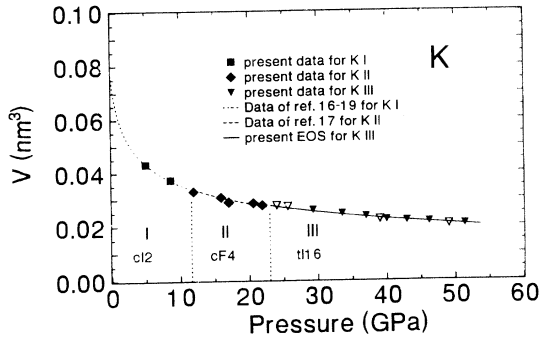

FIG. 3. Atomic volume of K at ambient temperature and pressures between 0 and 51 GPa. Open symbols mark decreasing pressure points. Different phases are separated by vertical lines.

sure range, all the observed d spacings cannot be indexed satisfactorily by the previously proposed structure.[14] Present tests of indexing for this phase include cubic, hexagonal, and tetragonal systems with up to 16 atoms per unit cell, as well as the orthorhombic system with up to eight atoms per unit cell. Only one tetragonal-body-centered lattice with 16 atoms per unit cell $tI16$ gives satisfactory indexing as shown by the calculated line pattern in Fig. 1. The lattice parameters for this structure are $a=953.2(7)$ pm, $c=457.1(3)$ pm, c/a ratio$=0.480(1)$ with an atomic volume $V=0.025\,98(4)$ nm^3/atom at 29.3(15) GPa.

For the measured region of the d values from 100 to 350 pm a comparison of observed and calculated values is shown in Table I for this lattice type and a spectrum taken at 29.3 GPa. All observed diffraction lines are indexed thereby with deviations in the d values of less than 0.4%; however, not all the lines allowed by this lattice type are actually noticed at the present intensity to background level. Especially above 40 keV, many lines are calculated but not observed unambiguously; however, the large number of atoms in the unit cell of the $tI16$ structure can lead to many weak lines, which could be hidden still in the background of the present technique.

The finite intensity for (310) and (222) requires that the apparent extinction of (330) and (510) do not correspond to systematic extinction, and therefore there are yet 12 possible space groups. The further selection of the special atomic positions depends on the clearly notified texture. With the present spectra any further speculations about possible space groups and structures must be de-

TABLE II. EOS parameter values for the phases K I to K III. The quoted "restricted" uncertainties represent only the statistical uncertainties of uncorrelated parameter variations (Ref. 21).

Phase	V_0 (nm^3/atom)	K_0 (GPa)	K_0'
K I	0.075 65	2.963(1)	4.06(19)
K II	0.071(16)	4.2(5)	3.6(3)
K III	0.060(8)	8.8(5)	3.1(1)

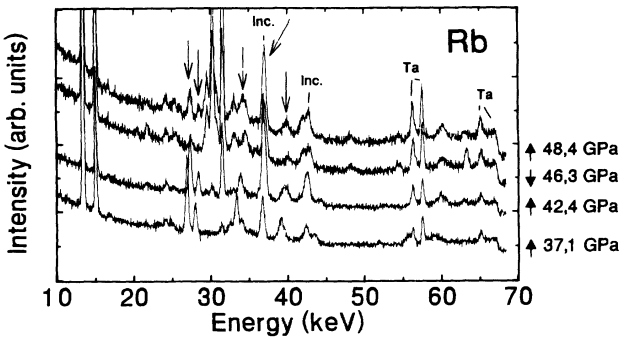

FIG. 4. EDXD spectra of Rb between 37 and 49 GPa. Diffraction lines of the Rb V structure in Rb VI are marked with arrows in the figure. The arrows on the right-hand side mark increasing and decreasing pressure.

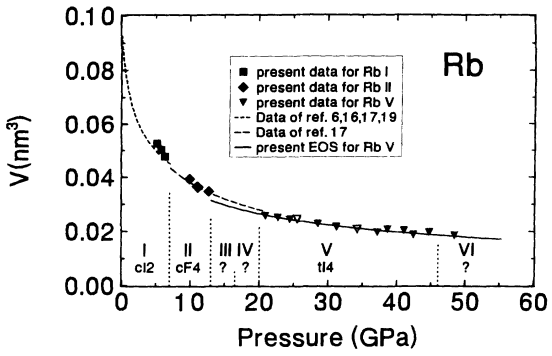

FIG. 6. Atomic volume of Rb at ambient temperature and pressures between 0 and 50 GPa. Open symbols mark decreasing pressure points. Different phases are separated by vertical lines.

layed until the new technique of spinning the sample during the measurement[15] is also applied to this case for reduction the texture.

The pressure dependence of the d spacings is shown in Fig. 2, and it is noticed that the $tI16$ structure gives satisfactory results for the K III phase up to the present maximum pressure of 51.4 GPa for both increasing and decreasing pressure. Figure 3 shows the effect of pressure on the atomic volume V at ambient temperature, whereby the $tI16$ indexing is used for K III. The dashed curves represent the best fit for the low-pressure data from the literature[16–19] in good agreement with the present results. A least-squares fit of the present data for K III is represented by the solid curve using the analytic form[20]

$$p=\frac{3K_0}{x^5}(1-X)e^{(3/2)(K_0'-3)(1-X)}$$

with $X=(V/V_0)^{1/3}$, whereby V represents the atomic volume at the given pressure p, and the fit parameters V_0, K_0, and K_0' stand for the volume, bulk modulus, and its pressure derivation at ambient pressure or extrapolated to $p=0$.

The best-fit results for these values are given in Table II. It should be noticed that an extrapolation of the fitted curves beyond the stability range of the individual phases has limited meaning and the given uncertainties of the "extrapolated" fit parameters reflect only statistical errors for uncorrelated parameter changes. Therefore, the apparently larger values for V_0 of some high-pressure phases illustrate only the uncertainties of such extrapolations. Indeed, if one would fix the values of V_0 for the high-pressure phases to the known value of the low-pressure phase, one would also obtain different values for K_0 and K_0' of the high-pressure phases. But there is no justification for this procedure, and the present values represent just the result of the three-parameter fit.

Rubidium. In addition to the well-known phases Rb I–Rb V in the pressure range up to 42 GPa, a new structure was observed on increasing pressure at about 46 GPa. Changes in intensity for the peaks of this new phase with respect of the peaks of the $tI4$ structure type of Rb V are illustrated in Fig. 4 for a few steps on increasing and decreasing pressure. One can notice in this figure that the diffraction lines of Rb V disappear step by step and the new lines for Rb VI grow out of the background. An attempt to index this new structure has not yet been successful, but the large number of diffraction lines also with large d values herald a new structure of low symmetry with a large unit cell.

The effect of pressure on the d values of rubidium in its different structures is shown in Fig. 5 for increasing and decreasing pressure. Obviously the phase transition into the new Rb VI structure exhibits a strong hysteresis over the range from 37 to 50 GPa at least.

The variation of the atomic volume is shown in Fig. 6,

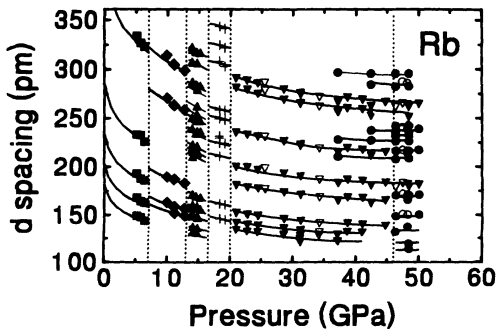

FIG. 5. Pressure dependence of d spacings for Rb. The solid and open symbols mark data for increasing and decreasing pressure, respectively.

TABLE III. EOS parameter values for the phases Rb I, Rb II, and Rb V. The quoted "restricted" uncertainties represent only the statistical uncertainties of uncorrelated parameter variations (Ref. 21).

Phase	V_0 (nm³/atom)	K_0 (GPa)	K_0'
Rb I	0.092 74	2.301(3)	4.1(3)
Rb II	0.081(11)	5.8(3)	2.00(8)
Rb V	0.093(6)	1.92(5)	3.42(7)

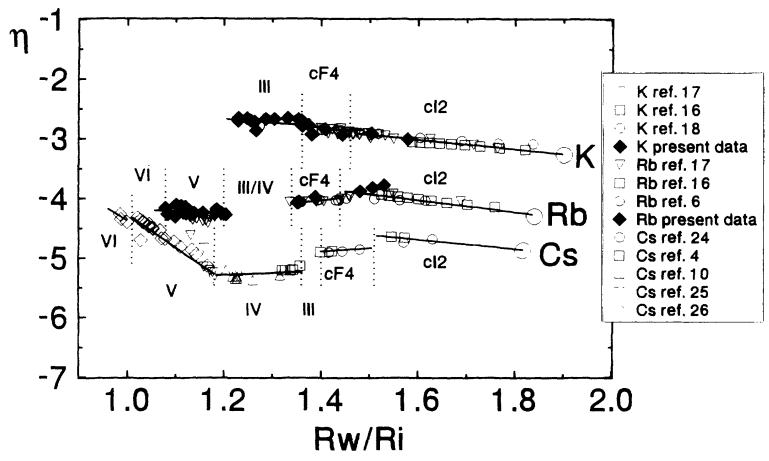

FIG. 7. EOS data for the heavy alkali metals in η representation with $\eta=\ln(P/P_{FG})-\ln[1-(V/V_0)^{1/3}]$ using the Fermi-gas pressure p_{FG}. Rw/Ri is the scaled Wigner-Seitz radius. The solid and open symbols are present data and literature data, respectively. Different phases are separated by vertical lines. The great open circles are the zero pressure values of Refs. 19 and 27.

where the dash curves represent earlier literature data[6,16,17,19] fitted by the same equation-of-state (EOS) form used also for the potassium data. The extrapolated curves for Rb II and Rb V into the region of Rb III/IV represent the upper and lower limits, respectively, giving narrow constrains on further indexing schemes for these more complex structures. In the same way, the extrapolated values for Rb V into the region of Rb VI also constrain the EOS data for this unknown structure. The best-fitting parameters are given in Table III for the different phases of rubidium, and, as in case of potassium, the parameter values are strongly correlated.

EQUATION-OF-STATE DATA

For a more detailed evaluation of the present experimental EOS data together with earlier literature data,[4,6,10,16–18,24–27] Fig. 7 presents a useful "linearization," whereby the scaled stress variable,[20,22]

$$\eta=\ln\left[\frac{p}{p_{FG}}\right]-\ln\left[1-\left[\frac{V}{V_0}\right]^{1/3}\right]$$

is plotted versus the radius ratio of the pressure dependent Wigner-Seitz radius Rw with respect to the constant ionic radius Ri. Thereby $p_{FG}=a_{FG}(Z/V)^{5/3}$ represents the pressure of a Fermi gas with Z electrons in the atomic volume V and

$$a_{FG}=\frac{(3\pi^2)^{2/3}}{5}\frac{\hbar^2}{m_0}=23.369\ \text{MPa nm}^5$$

is a universal constant.

As discussed previously in much more detail[20,22,23] the EOS data are plotted in such a way that the limiting behavior at very strong compression, given by the Thomas-Fermi gas, and at small compression, given by Hook's law, is interpolated by a straight line in the case of "simple" solids. A linear interpolation is therefore considered as the "regular" behavior. In contrast to this regular behavior, a minimum is observed in the case of cesium with a sharp break at Rw/Ri=1.2. Below this value the curve is linear and has a steep slope. This indicates a regular behavior. The behavior of rubidium is similar to cesium, but the anomalies are weaker. Potassium shows nearly linear behavior over the whole present pressure range, however, also with very small slope. The almost flat curves for the phases II–IV for cesium, II–V for rubidium, and II–III for potassium are typical for continuous electronic changes referred to the *s-d* transfer in these "incipient transition metals" under pressure. The break in the slopes for cesium and rubidium points to the completion of the *s-d* transfer. Different strength in the anomalies of these metals are due to the fact that these anomalies occur in the lighter elements just at higher pressures but still almost at the same radius ratio Rw/Ri.

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