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High-pressure phase transitions in potassium and phase relations among heavy alkali metals

K. Takemura* and K. Syassen
Physikalisches Institut III, Universität Düsseldorf,
D-4000 Düsseldorf 1, Federal Republic of Germany

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The optical reflectivity ($0.5\ \mathrm{eV} \leq \hbar\omega \leq 5\ \mathrm{eV}$) of potassium metal has been measured to 380 kbar at room temperature. Two phase transitions occur at 114 and 188 kbar, respectively. By comparison to the high-pressure optical properties of Cs and Rb the phase K-II has fcc structure. At 188 kbar, K undergoes a considerable change in its optical response indicating the occurrence of a complicated Fermi-surface topology. The phase transitions in K, together with recent experimental investigations of Rb and Cs, reveal systematic trends in the phase stability of heavy alkali metals under pressure.

The recent interest in the pressure-induced transfer of *s* electrons into *d*-like states arises from the discovery that *d* electrons play an important role in determining the crystal structure stability of elemental metals from the left-hand side of the periodic table. Ground-state energy-band calculations elucidate a close relationship between *d* occupation number and systematic trends in phase stability—not only for transition metals and the lanthanides, but also for the third-period metals Na through Al (Ref. 1) and the alkaline earths (Ref. 2). Similarly, a systematic sequence of phase transitions is expected to occur in the pretransition metals K, Rb, and Cs.

The $s \rightarrow d$ transfer in Cs results in a considerable volume reduction ($V/V_0 - 0.28$ at 100 kbar) and an abundance of phase transitions, which have been extensively studied both experimentally and theoretically.[3,4] More recently, Rb was shown to undergo four phase changes below 250 kbar.[5-7] The only experimental evidence (isothermal conditions) for a high-pressure phase transition in K at about 260 kbar stems from low-temperature electrical resistance measurements by Stager and Drickamer.[8] Bukowinsky has theoretically investigated the $s \rightarrow d$ transfer in K (bcc structure only) with main emphasis on geophysical implications.[9]

In the present work, we report on the optical investigation of high-pressure phase transitions in K. At room temperature, two transitions occur below 380 kbar, one at 114, the other at 188 kbar. From the optical data we derive conclusions about the nature of the phase changes. The new results for K together with those for Cs (Refs. 3 and 4) and Rb (Refs. 6 and 7) enable us to outline systematic trends in the phase stability of heavy alkali metals under pressure. Also, we propose an explanation why the phase diagrams are not isomorphous for an intermediate degree of $s \rightarrow d$ transfer.

The optical reflectivity of K under pressure was measured in a diamond anvil cell using a microoptical system described elsewhere.[10] K metal of 99.95% nominal purity was loaded into the cell under argon atmosphere without using any pressure medium. The reflectivity was determined at the diamond-sample interface (hereafter called R_d). Pressures were obtained from the ruby fluorescence shift using a conversion factor 0.365 Å/kbar. In passing we mention the strong tendency of K to weaken Inconel or stainless-steel gaskets at pressures above 100 kbar. Thus, the need to work with thin gaskets (initial thickness $< 60\ \mu\mathrm{m}$) and small sample diameters ($< 70\ \mu\mathrm{m}$) prevented us from x-ray diffraction studies of the phase transitions in K by angle-dispersive methods.

Figure 1 shows pressure scans of the reflectivity of K at two different photon energies. In the 3-eV scan R_d decreases rapidly with a 12% discontinuity at 114 ± 2 kbar. The infrared reflectivity at 0.7 eV first decreases smoothly between 50 and 180 kbar. At 188 ± 2 kbar R_d drops to less than 10%. No further anomalies are detected up to 380 kbar. We infer that K undergoes at least two phase transitions below 380 kbar. We do not completely rule out any further transitions between 188 and 380 kbar, because changes in absolute reflectivity $\Delta R < 0.02$ would be difficult to detect with our present method. The pressure-induced changes of R_d are completely reversible. A possible hysteresis is less than 3 kbar for both transitions.

Figure 2 shows some reflection spectra measured from 0.5 to 5 eV at pressures close to the phase transitions. The spectrum at the lowest pressure of 5 kbar compares favorably with R_d calculated from experimental optical constants at normal volume.[11] This comparison rules out any significant surface contamination in the present experiment. On raising the pressure to 111 kbar, R_d decreases continuously and an edge develops between 1 and 2 eV. At 115 kbar just above the first transition the edge broadens and the bottom

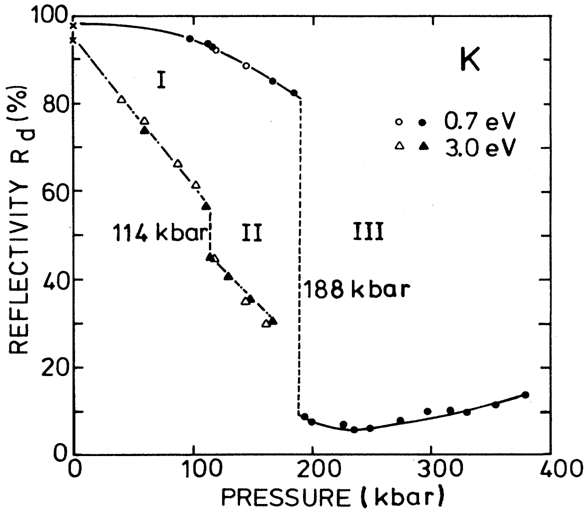

FIG. 1. Pressure scans of the optical reflectivity of K metal at 0.7 and 3.0 eV. R_d corresponds to reflectivity at the diamond-sample interface.

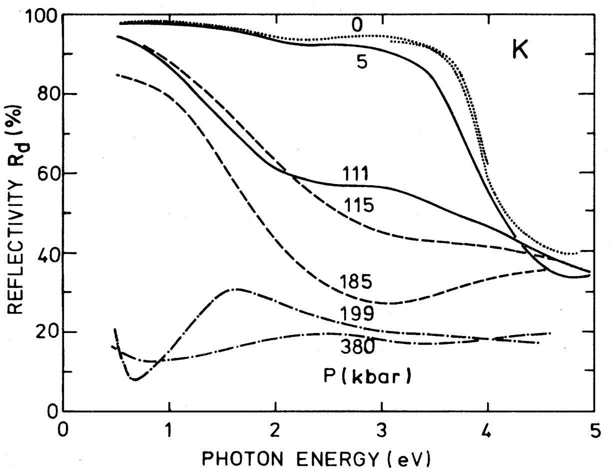

FIG. 2. Reflection spectra of K metal at several pressures in the pressure range 0–380 kbar. Solid, dashed, and dash-dotted lines correspond to phases I, II, and III, respectively. For comparison, reflection spectra calculated from optical constants at normal pressure (Ref. 11) are also shown (dotted lines).

point of the edge moves to 3 eV. The overall decrease of R_d continues in the phase K-II up to the second transition. The change of the reflectivity at the second transition is quite dramatic. The small upturn of R_d at low energies is the only evidence for the metallic nature of K-III.

The analysis of some reflection spectra is given in Fig. 3 which shows the real part $\sigma(\omega)$ of the optical conductivity. The results were obtained from Kramers-Kronig transformation as well as from fitting phenomenological expressions for free electron (Drude-type) and interband absorption to the experimental data. Though the absolute numbers for $\sigma(\omega)$ are uncertain to about ±20%, the spectral features are independent of the assumptions entering the analysis, i.e., extrapolation of R_d and sum-rule considerations.

The pressure dependence of R_d and $\sigma(\omega)$ in K-I and K-II is similar to the changes observed in the bcc and fcc phases of Rb and Cs.[12] In following the interpretation given in Ref. 12, the decrease of the reflectivity is attributed to the $s \rightarrow d$ transfer in the lowest conduction band and the associated increase of the optical interband absorption. At the I → II transition the peak in $\sigma(\omega)$ shifts from 2.0 to 3.1 eV. Similar peak strengths and peak shifts have been observed for Cs and Rb at their bcc-fcc transitions (1.2 to 1.8 eV in Cs, 1.7 to 2.5 eV in Rb). For Cs and Rb, the spectral change in the optical absorption reflects characteristic changes in the joint density of states at the structural bcc-fcc transition. The striking similarity of the optical response of K strongly suggests that the phase K-II also has the fcc crystal structure.

The first phase transition in K fits smoothly into the sequence of bcc-fcc transition pressures and volumes of the heavy alkali metals. Figure 4 shows the metallic radii of the alkali metals near high-pressure phase transitions. Metallic radii of K are estimated by extrapolating isothermal compression data[15] using a Birch equation. Obviously, there is a comparable region of stability for the fcc phases in Cs, Rb, and K. High-pressure x-ray diffraction studies by Alexandrov *et al.*[14] have proved that the bcc phase of Na, which has no *d* states close to the Fermi level E_F at normal volume, is stable up to at least 300 kbar. Also, in our optical observations of Na we could not detect any phase changes below 350 kbar. According to the generalized pseudopotential theory of Moriarty and McMahan[1] the stability of the bcc phase of Na extends to about 1 Mbar, at which pressure the hcp phase may become more stable than fcc.

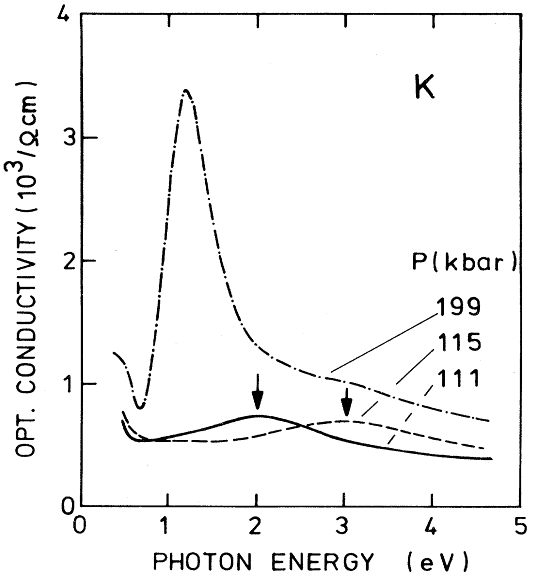

FIG. 3. Optical conductivity (real part) of K metal for the phases K-I at 111 kbar (solid line), K-II at 115 kbar (dashed line), and K-III at 199 kbar (dash-dotted line).

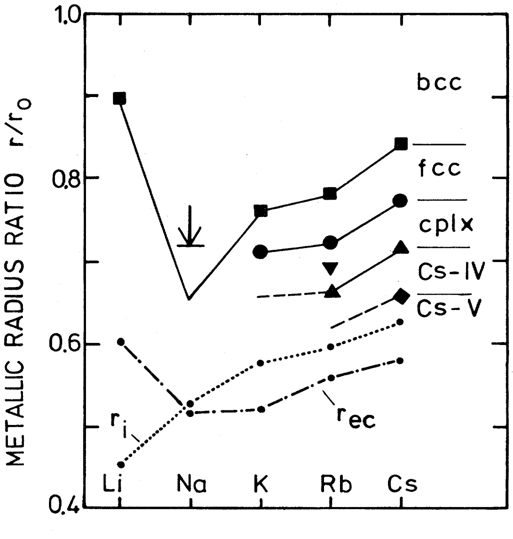

FIG. 4. Metallic radius ratio normalized to the zero-pressure value r_0 (converted to bcc lattice, coordination number 8) for the alkali metals at their high-pressure phase transitions. Data are from Ref. 4 (Cs), Refs. 6 and 7 (Rb), present work (K), and Ref. 13 (Li). According to Ref. 14, there is no experimental evidence for a phase transition in Na up to $r/r_0 = 0.74$ (marked by arrow). Ionic (r_i) and empty core radii (r_{ec}) at normal volume are shown for comparison. Note that the metallic radius of Cs-IV (see Ref. 4) approaches the ionic radius.

The results of not finding a phase transition in Na below 300 kbar ($V/V_0=0.40$) supports the argument[12] that the bcc → fcc transition in the heavy alkali metals including K is closely related to the degree of s-d transfer in the lowest conduction band. We note, however, that core interactions[16,17] may not be negligible in a detailed theoretical analysis of the phase stability of K. The large stability range of bcc-Na is furthermore taken as evidence that the mechanism for the bcc → fcc transition in Li reported by Olinger and Shaner[13] is different from the heavy alkali metals.

We now turn to the second transition in K. A two-band nature of the conduction states with mainly d character near E_F would partly account for the low reflectivity of K-III: Efficient intra- and interband scattering across the Fermi surface (FS), together with a large effective mass of d electrons, significantly changes the free-carrier contribution to the dielectric response. A dominant feature, however, is the pronounced peak in $\sigma(\omega)$ near 1.2 eV (see Fig. 3). This peak is attributed to interband transitions. The strong low-energy interband absorption is clear evidence for an optical gap over extended regions of the Brillouin zone and for a large density of occupied states close to E_F.

Since general trends in the electronic structure of heavy alkali metals under pressure are qualitatively similar, it is tempting to relate the 188-kbar transition in K to the fact that in the fcc phase a second d subband of X_3 symmetry starts to drop below E_F. In Cs, this FS anomaly is believed to initiate the isostructural volume collapse at the Cs-II → Cs-III transition near $V/V_0=0.46$.[3,18,19] Nonrelativistic energy-band calculations for fcc Cs (Ref. 19) obtain a van der Waals loop in the pressure-volume relation at $T=0$ K, while in the relativistic case[3] thermal effects account for an fcc → fcc transition above some critical temperature. A van der Waals loop in fcc K arising from the occupation of the X_3 level is difficult to imagine, since the repulsive pressure due to the *sp* electron density is much larger as compared to Cs. Consequently, we rule out a first-order fcc → fcc transition in K at 188 kbar and consider a change in crystal structure.

The instability of the fcc phase of K is possibly related to a second characteristic FS feature of the heavy alkali metals. The $s \rightarrow d$ transfer in the lowest conduction band results in the formation and subsequent disruption of 100 necks inside the first Brillouin zone (BZ). For FS pictorial representations the reader is referred to Refs. 20 and 21. A shrinkage of the neck radius means a loss of occupied states near E_F and a faster rise of the total energy with decreasing volume.[19] The disruption of the neck occurs near a wave vector which is approximately one half of the Γ-X distance. For states close to the neck it would be energetically more favorable to double the unit-cell dimensions or, in other words, to introduce a new BZ boundary at $\frac{1}{2}k_{\Gamma X}$. The splitting of states at this new boundary is likely to moderate the total energy increase due to the shrinkage of the neck. However, the mechanism is certainly complicated through zone folding effects such as, e.g., additional splittings at the BZ center.

Though the explanation for the instability of the fcc phase must be regarded as tentative, it gains support from the fcc to tetragonal[4] transition in Cs. This transition can be viewed as a doubling of the lattice parameter in just one of the three equivalent [100] directions. The transition is obtained by displacing subsequent 100 layers of the fcc phase in directions perpendicular to [100].

The disruption of the 100 neck in fcc Cs occurs after the X_3 level has passed through E_F. For K it is conceivable that effects arising from the two characteristic FS anomalies accumulate near the same volume, because the X_1-X_3 splitting in K is larger compared to Cs (Ref. 22) and relativistic shifts of energy levels[3] are less important. It is then the difference in volume between the occupation of the X_3 level and the disruption of the 100 neck which (in addition to the difference in s and p partial pressures) accounts for the fact that the phase diagrams of the heavy alkali metals are not isomorphous in the intermediate radius range denoted "complex" in Fig. 4. Olijnik and Holzapfel[7] identified the crystal structure of Rb-V to be of the "Cs-IV" type.[4] This result indicates that beyond the complex region and for a large degree of $s \rightarrow d$ transfer the phase diagrams become isomorphous again. The crystal structures of Rb-III and Rb-IV (128–190 kbar) are unknown. The low reflectivity of Rb-IV (Ref. 6) points out a possible phase relation to K-III.

The above discussion of the phase sequence in the heavy alkali metals is entirely based on room-temperature experimental data. Since the Gibbs free energy governs phase transitions, we also have to consider the effect of temperature on the phase boundaries. In this regard the low-temperature studies of K by Stager and Drickamer[8] are not helpful. This is at least partly due to problems arising from different pressure scales. We have to await new investigations in particular of Rb and K to see the importance of the temperature variable.

In conclusion, two phase transitions in K at room temperature are discovered by the present optical experiments. The interpretation of the optical response together with recent x-ray diffraction results for Cs (Ref. 4) and Rb (Refs. 6 and 7) enable us to recognize some systematic trends in the phase sequence of the heavy alkali metals under pressure. We give a tentative explanation why the phase diagrams are not isomorphous for an intermediate degree of s-d transfer. In order to substantiate and further unravel the phase relations between K, Rb, and Cs, crystal structure determinations of the phases Rb-III, Rb-IV, and K-III would be most helpful.

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[*] Present address: The Institute for Solid State Physics, The University of Tokyo, 7-22-1 Roppongi, Minato-ku, Tokyo 106, Japan.

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