pl3 **Structural Phase Transitions of Simple Metals under Pressure***. K. Syassen, *Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-70569 Stuttgart*. Keywords: high pressure, alkali metals, phase transitions.

The alkali metals have played an important role in developing the nearly-free electron picture for simple *sp* band metals. With increasing pressure, however, these metals become less free-electron like. For instance, at sufficiently high density (3- to 5-fold compression) the heavy alkali metals K, Rb, and Cs essentially turn into monovalent *d* transition metals. The pressure-driven $s \rightarrow d$ transition, which implies a spatial redistribution of valence electrons, is considered to be the driving force for destabilizing the common high-coordination low-pressure structures (*bcc* and *fcc*) with respect to more open structures. In fact, it has been known for some time already that at intermediate densities both Rb and Cs adopt an unusual body centered tetragonal structure (Z=4), where the atoms are only eightfold coordinated. The existence of a variety of other high pressure phases has been inferred from optical reflectivity measurements, electrical transport studies, and x-ray diffraction measurements. Solving the crystal structures of most of these other high-pressure modifications has remained a long standing problem.

In this contribution we mainly discuss results of recent high pressure structural studies (P < 100 GPa) of alkali metals [1-5]. The diffraction experiments were carried out at the ESRF Grenoble. The metals were compressed using diamond anvil cells. The x-ray diffraction patterns (wavelength near 0.45 Å) were recorded on a flat image plate detection system. Indexing, structure solution, and refinements of diffraction diagrams were performed using standard crystallography procedures. Both, the high angular resolution and the high sensitivity of the experimental setup were essential for being successful in solving low-symmetry crystal structures.

As for the heavy alkali metals, the most striking results are the observation of a Cmca phase with 16 atoms per cell in Cs and Rb [1,2] and, in particular, an I4/mmm phase of Rb [3] with about 19.5 atoms per basic tetragonal cell. In the latter case, a subset of Rb atoms forms a framework with channels which are occupied by incommensurate chains of a second set of Rb atoms.

More recently, the high pressure behavior of Li has become of prominent interest, partly because it is the monovalent element closest to hydrogen in the Periodic Table. In the case of Li the trend towards low-coordination phases starts at about 40 GPa. We have discovered two new low-coordination high-pressure phases of Li [5]. Formation of these phases in Li can be related to the increasing p character of the valence electrons with increasing density.

We compare the structural behavior of alkali metals under pressure to results of total energy calculations and structure optimizations based on first-principles band structure methods. These provide insight into changes in electronic properties and chemical bonding. Furthermore, we point out striking resemblances between the new structures found for alkali metals and three-dimensional nets formed by cations or anions in binary transition metal silicides and phosphides. A few related experimental and theoretical studies of alkalis and other elements will be touched briefly [6-8].

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