FIGURE 1. Schematic configuration coordinate diagram.

ture, accompanied by a volume discontinuity, i.e. it may involve a first order transition. Alternatively, the two states may be present over a large range of pressures with the amount of conversion changing with pressure as in a chemical equilibrium. The bulk of this article is devoted to a discussion of electronic transitions, their physical and especially their chemical consequences. In the first section, we discuss electronic transitions in alkali, alkaline earth, and rare earth metals. Then we mention briefly insulator-metal transitions. The third section describes the chemical consequences of electronic transitions in aromatic hydrocarbons and their complexes. Finally, we discuss at some length a variety of changes in the electronic structure of ferric and ferrous iron. All these electronic transitions involve a degree of interaction among adjacent sites; in the metals the interactions extend throughout the lattice. These have in common, however, the feature that they are in some sense describable in terms of the states of the individual atoms or molecules. We omit from this discussion such purely cooperative phenomena as transitions between paramagnetic and ferromagnetic or antiferromagnetic states.

METALS

The concept of the electronic transition was first applied to metals. Some twenty-five years ago Bridgman discovered a volume discontinuity (21) and a cusp in the resistance (22) of cesium near 40 kbar. Since cesium transforms from bcc to fcc at 22 kbar, Sternheimer (23) proposed that the event at 40 kbar involved the promotion of the $6s$ electron to the $5d$ shell (or rather, a change from s to d character in the conduction band). While his calculations were approximate, it appears that his analysis is basically sound. Hall, Merrill & Barnett (24) have demonstrated by means of X-ray measurements that there

are two closely spaced volume changes associated with the 40 kbar transition, but that the structure remains fcc. After 1960 a considerably larger pressure range became available. It was then discovered that the resistance started to rise again near 100 kbar, and exhibited a maximum near 135 kbar (25, 26) (see Figure 2). There are speculations that the higher pressure transition introduces *f* character to the conduction band, but no really satisfactory analysis has been performed. It is of considerable interest that the phase present above 100 kbar is superconducting, as shown by Wittig (27). This is the first example of a superconducting alkali metal, a phenomenon which at one time was considered impossible.

Rubidium has a transition near 60 kbar, apparently from the bcc to the fcc structure. Near 145 kbar there is a very sharp rise in resistance (1, 28, 29) as shown in Figure 2. This would appear to be associated with an electronic transition changing the conduction band character from $5s$ to $4d$. The maximum near 300 kbar may be associated with a further electronic rearrangement.

At room temperature potassium (29) exhibits only a continuous increase in resistance with pressure above about 20 kbar (by a factor of 30–40 in 500 kbar). This is in itself anomalous, as most metals exhibit a modest decrease in resistance with increasing pressure due to reduced amplitude of the lattice vibrations. At 78°K there is a sluggish transition at 230–240 kbar, probably from bcc to fcc structure, then a very sharp rise in resistance near 280 kbar (see Figure 3). The magnitude of the rise decreases with increasing temperature, so that it disappears near 250°K. The sluggish transition at lower pressure is not observed either. The sharp transition could well be the $4s \rightarrow 3d$ electronic
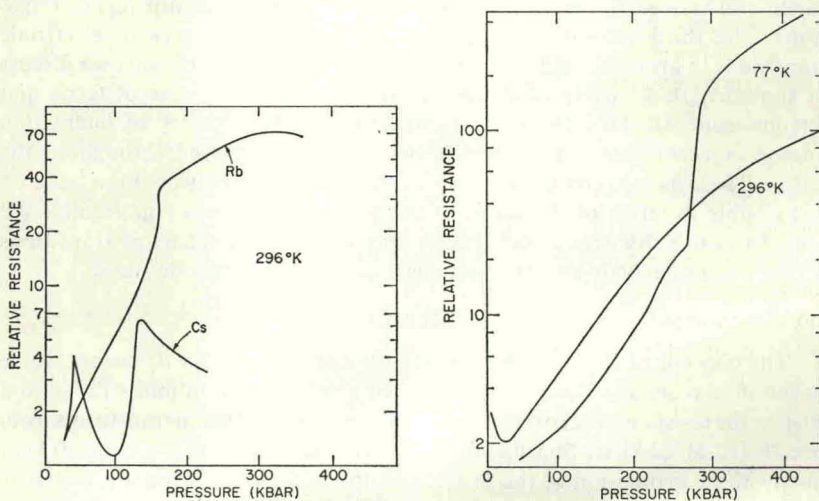

FIGURE 2 (*left*). Resistance vs pressure—cesium and rubidium.

FIGURE 3 (*right*). Resistance vs pressure—potassium.