

FIG. 2. Dependence of the electrical resistance of Cs on pressure.<sup>[22]</sup> The pressure scale should be corrected for Bridgman's curve (Br):<sup>[31]</sup> 100 kbar on the old scale corresponds to 80 kbar on the new scale.

Cs IV.<sup>[23]</sup> The chain curve in the region of 175 kbar in Fig. 1e shows part of the boundary between the high-pressure phases, found from the electrical resistance discontinuities and reported in<sup>[24]</sup>.

X-ray-structure analysis under pressure was used to determine the crystal structures of the modifications Cs II and Cs III.<sup>[22]</sup> It was found that the initially bcc lattice was transformed under pressure into a more closely packed lattice: the fcc lattice of the copper type (type A1) with a lattice constant  $a = 5.984 \pm 0.01 \text{ \AA}$  (at 41 kbar). Further increase in pressure produced a new modification at 42.4 kbar, with the same crystal structure (fcc type A1) but with a smaller lattice parameter:  $a = 5.800 \pm 0.007 \text{ \AA}$  (at 42.5 kbar). Calculations showed that an isomorphous transition in cesium in which the crystal structure was retained could have been the result of an internal rearrangement within the atoms, i.e., the result of a transition of the valence electrons from the 6s- to the 5d-state.<sup>[5,32]</sup>

An electronic transition accompanied by the isomorphous A1  $\rightarrow$  A1 transformation has been found in one other element: the rare-earth cerium, in which pressure produces an electronic transition from the 4f- to the 5d-state.

Debye diffraction patterns of the Cs IV modification were reported also in<sup>[22]</sup>, but in this case it was not possible to index reliably the diffraction reflections. The patterns obtained suggested that this modification had stacking faults or an hcp structure with twin c-axes, similar to that observed in rare-earths of the lanthanum type (type A3').

In connection with this, it should be mentioned that the fcc type A1 structure, the hcp magnesium type (A3) structure, and the lanthanum (A3') structure are all very similar in their packing of the layers. This

can be understood by considering Figs. 3 and 4, which show unit cells for these three structures. Thus, the high-pressure modification Cs IV is very likely to have the hcp type A3 structure.

Rubidium has physical and chemical properties which are very similar to those of cesium and it may have a P-T phase diagram similar to that of cesium. If this is correct, the rubidium diagram should have a form close to that shown in Fig. 1d. The same is true of potassium: so far, we know only a part of its fusion curve up to 60 kbar<sup>[27]</sup> and two points at which electrical resistance discontinuities have been observed.<sup>[28]</sup> Here and later, we shall use dashed curves to denote probable phase boundaries.

Lithium and sodium probably have simpler diagrams due to the simpler structure of their atoms. The boundary between phases I and II of lithium and sodium intersects the temperature axis, and the low-temperature phase has been investigated at atmospheric pressure. X-ray diffraction analysis showed that after a polymorphic transition, these metals had the hcp type A3 lattice, similar to that of magnesium.<sup>[29]</sup>

Compared with the initial bcc structure, the A3 lattice is more compact with a packing factor  $\varphi = 0.74$ .

### 3. ALKALINE-EARTH METALS OF GROUP II-A

We shall consider the elements of group II-A in the

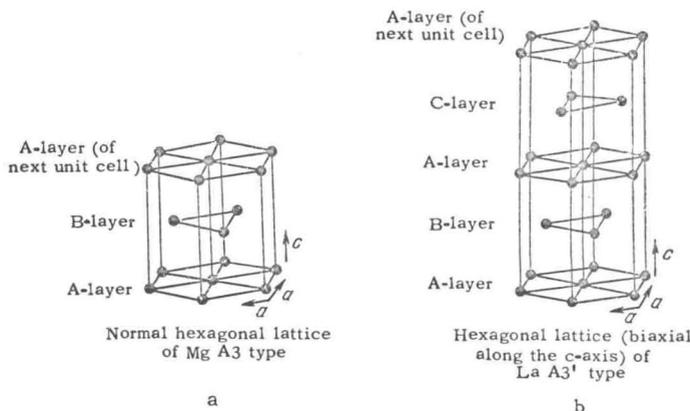


FIG. 3. Distribution of atoms in hcp structures of the Mg A3 type (a) and of the La A3' type (b).

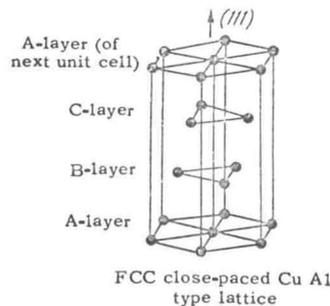


FIG. 4. Distribution of atoms in the fcc Cu A1 type structure. Unit cell is shown in hexagonal axes.