

*SOME RELATIONSHIPS GOVERNING THE P-T PHASE DIAGRAMS
AND POLYMORPHIC TRANSFORMATIONS OF ELEMENTS UNDER HIGH PRESSURES*

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1. INTRODUCTION

CERTAIN properties of substances, such as their compressibility, melting point, thermal expansion coefficient, etc., exhibit, under normal conditions, a periodic dependence on the atomic number of the element.

Vereshchagin and Likhter^[1] and, later, Ryabinin^[2] showed that the general nature of the periodicity was retained up to pressures of 500 kbar, but with further increase in the pressure the periodic curve gradually smoothed out so that at very high pressures it became a monotonic function of the atomic number.^[3] In other words, at very high pressures, elements cease to differ from one another in their chemical and physical properties.

It is known that two-thirds of the elements in the periodic system have atoms with unfilled inner shells and, as found experimentally, pressure is capable of transferring electrons to vacant levels of higher energies. Since different energies are needed to achieve these electronic transitions in different elements, they naturally occur at different pressures. The lowest pressure for an electronic transition known at present is that of cerium; an electronic transition from the 4f-state into the 5d-state takes place at only 7 kbar. A discontinuous change in the structure of the energy spectrum of electrons is accompanied by a discontinuous change in the electrical conductivity so that discontinuities in the electrical resistance under pressure may indicate electronic transitions. However, it must be stated that a discontinuous change in the electrical conductivity also accompanies a polymorphic transition in a substance, which is a change in the crystal lattice. X-ray-diffraction analysis, by means of which we can estimate the atomic volume before and after a transition, helps us to identify an electronic transition. For example, in the case of cerium, x-ray analysis shows that under a pressure of 7 kbar a discontinuous change in volume by 7.7% is not accompanied by a change in the crystal lattice: it remains fcc. However, an estimate of the ionic radii shows that for the same transition the ionic radius jumps from 1.85 to 1.71 Å.^[4]

It is quite likely that the 42.5 kbar transition in cesium is also electronic. Cesium occupies a special place among other elements in that the 6s-, 5d-, and 4f-states of its electrons are extremely close in their energy values. It has been calculated that a pressure of 45-50 kbar should be sufficient to transfer the only

outer electron of cesium from the 6s- to the 4f-state and thus to convert cesium from a metal into an insulator. With further increase in the pressure, this electron may go over to the 5d-state and then cesium should again become a metal.^[5] It is evident from Fig. 2 that a sudden rise in the electrical resistance is indeed observed at 42.5 kbar and that it is replaced by a sharp drop when the pressure is increased slightly.

In principle, electronic transitions are possible in all elements having unfilled levels. Theoretical calculations give estimates of 10-100 kbar for electronic transitions. It is obvious that the change in the structure of an atom induced by an electronic transition will lead to a complete change in the chemical properties since these are governed by the electronic structure of the outer shells. Under high-pressure conditions, we would expect a somewhat different periodic table of elements since the change in their properties will affect the positions of the elements in the periodic table.^[6]

A further increase in the pressure will lead to the destruction of the electronic shells and the substance will go over to a plasma state with fixed positions of ("bare") nuclei or nuclei having electronic shell residues. Various theoretical estimates give different values for the pressures at which atoms and a crystal lattice would be destroyed. Relatively recent calculations made by Abrikosov^[7] showed that the crystal lattice should be conserved at pressures up to 100,000 kbar, and that, when very highly compressed, all elements should have the same crystal lattice with the highest binding energy. At present, it is difficult to predict the type of lattice which strongly compressed elements should assume: it may be bcc, or fcc, or hcp, with the ratio of axes in the latter satisfying the condition of maximum binding energy.

Thus, working even with maximum practically realizable pressures, we are still dealing with crystalline substances having a crystal lattice. The unique form of the lattice which a strongly compressed substance should assume can be deduced by observing the sequence of transitions from one crystal lattice to another in each of the elements in the periodic table, subjected to rising pressure.

A change in the external conditions (pressure or temperature) may, in certain cases, alter the equilibrium stable state of a substance, which corresponds to a minimum of the thermodynamic potential. Further