At a solid-solid phase transition there are rather spectacular optical effects, including a large discontinuous shift of the absorption edge. One can find out a good deal about electronic structure from a study of these discontinuities. Figure 8[2, 10] shows the shift of the edge vs pressure for several solids having phase transitions. The three silver halides are particularly interesting. AgCl and AgBr are much alike. Both are initially in the f.c.c. structure and show a very small shift of the edge with pressure. At 83,000 to 87,000 atm they show a phase transition, presumably to the SC (CsCl) structure accompanied by a large decrease in the energy gap. The high-pressure phase also shows a small shift with pressure. AgI, on the other hand, starts out in the zinc blende lattice, transforms at 4000 atm to the f.c.c. phase with a large decrease in gap, and shifts rapidly (like most ionic crystals) to 115,000 atm where there is a second phase change, presumably to the SC structure, accompanied by an increase of the gap. The high-pressure phase behaves like AgCl and AgBr. These peculiarities can be related to the unusual optical properties of the silver halides.

(b) Transitions Isolated at a Point in a Lattice. A most interesting set of electronic transitions are those where the ground state and excited state are both on the same entity (usually an atom or ion). The excitation may travel from atom to atom, but there is no electron transfer.

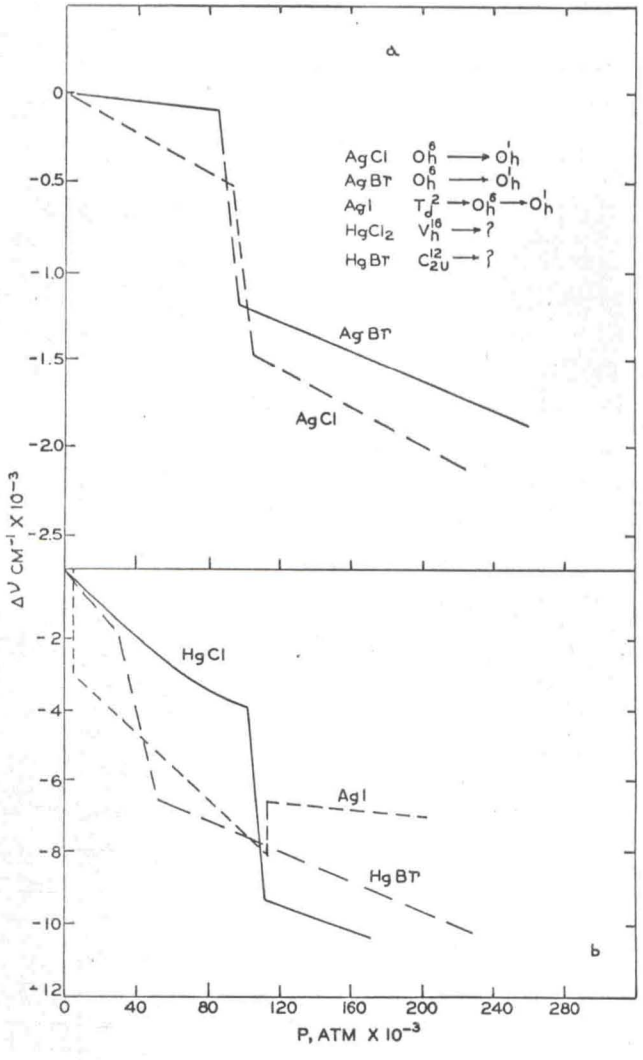

Fig. 8 Shift of the absorption edge at phase transitions.