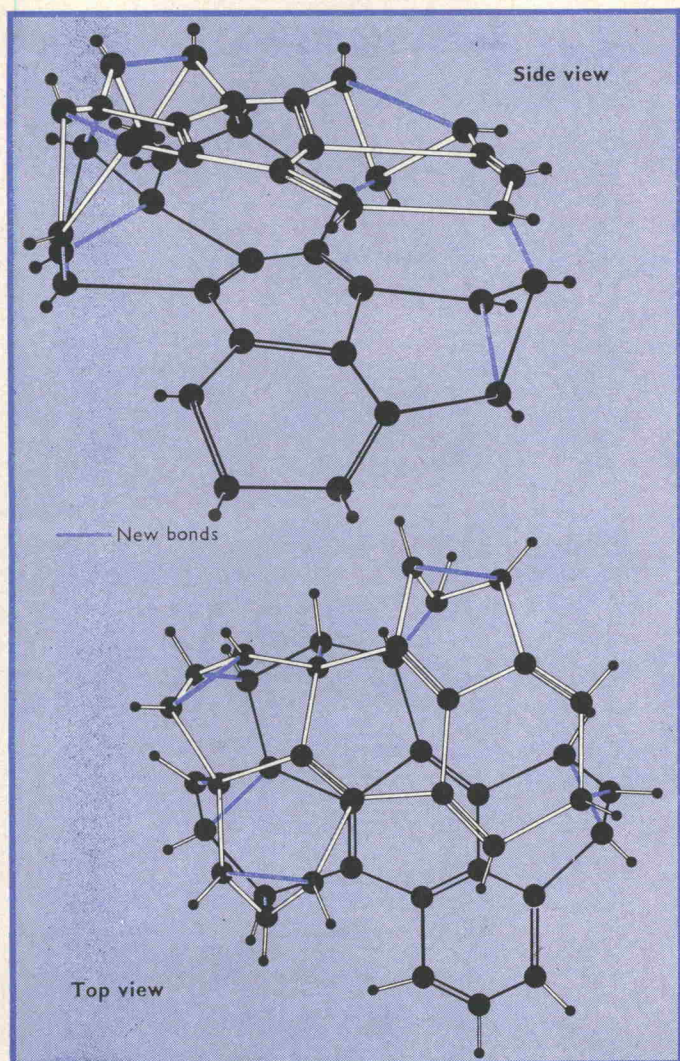


Fig. 4. (above) Change in relative resistance with pressure for rubidium and caesium at 296 K.

Fig. 5. (below) Structure of the perylene dimer formed at high pressure.



peak half width ($\delta E_{\frac{1}{2}}$) as follows:

$$E_{th} = h\nu_{max} - \frac{1}{RT \ln 2} (\delta E_{\frac{1}{2}})^2 \left(\frac{\omega}{\omega'}\right)^2 \quad 1$$

We shall see later that this equation gives reasonable qualitative predictions in a few cases where it has been applied.

Transitions in metals and insulator-metal transitions

These are the areas of most activity in physics. Resistivity can be defined as

$$r = \frac{1}{n\mu e}$$

where n is the number of carriers, μ their mobility and e their charge. Conduction in a metal is mobility limited. To the extent that mobility is limited by scattering due to lattice vibrations, we expect resistivity to increase with increasing temperature as vibrations are enhanced, and to decrease with increasing pressure, which inhibits vibrational amplitude. The expected temperature effect is observed, and, in simple metals like copper, the resistivity decreases by perhaps 20–40 per cent in several hundred kilobars. The conductivity ($1/r$) of insulators and semiconductors is controlled by the number of carriers, which, for simple cases, is:

$$n = n_0 \exp\left(\frac{-E_g}{2kT}\right)$$

where E_g is the gap between valence and conduction bands. E_g is a function of pressure. Since it generally decreases, a rapid decrease in resistivity with pressure is usually observed.

Electronic transitions were first discovered in metals. Nearly 25 years ago Bridgman found a cusp in the resistance of caesium near 40 kilobars (see Fig. 4). Sternheimer attributed this to donation of an electron from the $6s$ to the $5d$ band, *i.e.* a change in character of the conduction band. His analysis, while approximate, appears basically correct. In the last decade, a second maximum near 135 kilobars has been observed. Recent calculations indicate that there are two causes—a lowering in energy and broadening of the empty $4f$ band until it overlaps the conduction band, combined with hybridization of atomic $5p$ orbitals into the conduction band. One might say that with increasing pressure one goes from alkali to transition to rare-earth metal. The resistance of rubidium is also shown in Fig. 4. The sharp rise near 140 kilobars is the $5s \rightarrow 4d$ transition and the maximum near 300 kilobars may involve hybridization of $4p$ electrons into the conduction band. A number of rare earths exhibit unusual electrical behaviour which may in some cases involve transfer of an electron from $4f$ to the $5d$ band or to the conduction band. Electronic transitions of a somewhat different type are observed in calcium, strontium and ytterbium.

Insulator-metal transitions can occur in a number of ways. In molecular crystals, like iodine and a few aromatic hydrocarbons, it appears to happen by broadening and shift of the valence and conduction bands with no apparent structural discontinuity. In Si, Ge and their III–V analogues, it occurs discontinuously with a change to the white tin structure or its diatomic analogue. In some transition-metal oxides it occurs discontinuously by a mechanism very close to the electron-electron correlation proposed by Mott. McWhan and his associates at Bell Laboratories have done particularly effective studies on mixed V_2O_3 – Cr_2O_3 crystals. Jayaraman, also at Bell Laboratories, has shown that divalent samarium chalcogenides become metallic at high pressure