

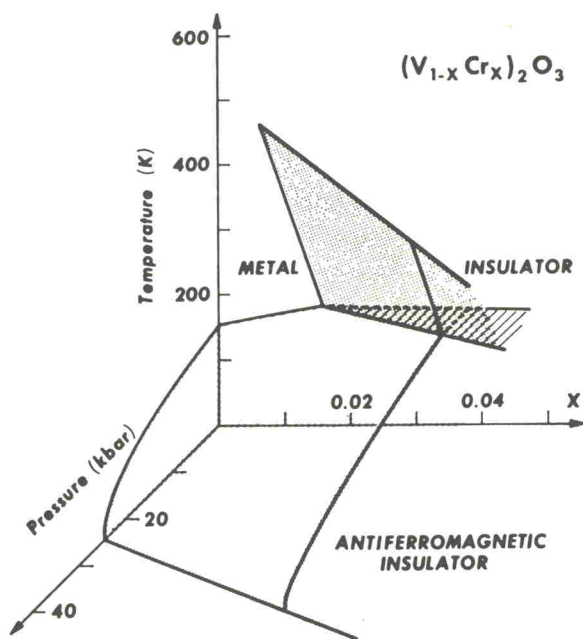


FIGURE 4. Pressure-temperature-composition phase diagram $V_{1-x}Cr_xO_3$.

mental. The work at Bell Laboratories has elucidated important concepts and presented an interesting class of materials.

AROMATIC CRYSTALS

Rather different electronic transitions occur in crystals of some aromatic hydrocarbons and in their charge transfer complexes with a variety of electron acceptors (62-66).

Aromatic hydrocarbons are planar molecules distinguished by their π orbitals which are conjugated to form an electron path around the molecular periphery. They form crystals of a characteristic herringbone structure. The ground state of the molecule is nonpolar and, in the solid at least, is rather unreactive. The excited states are polar and may be more reactive. The energy for optical excitation to the lowest excited state depends strongly on the length of the conjugated path. In anthracene, with three rings, $\nu_{\max}$ is at 26.4 kK (kiloKaysen); in tetracene, with four rings, it lies at 21.1 kK; and in pentacene, with five rings, it is at 17.1 kK. With increasing pressure the optical excitation energy decreases rapidly, as shown in Figure 5. ($V/V_0 = 0.7$ corresponds to about 50 kbar.) By 100 kbar the shift approaches 6-9 kK (0.8-1.1 eV). The electrical resistance also decreases with increasing pressure by 12-16 orders of magnitude in 300 kbar. Anthracene and tetracene remain semiconductors at

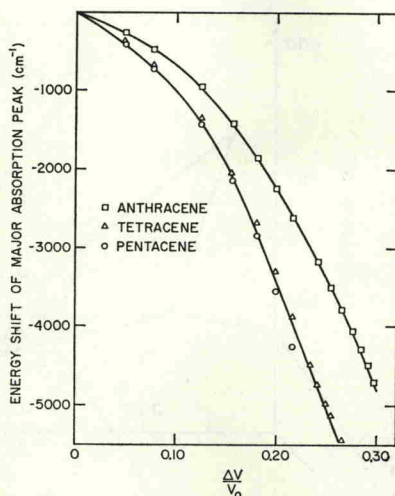


FIGURE 5. Shift of low energy optical absorption peaks with V/V_0 —aromatic hydrocarbons.

all available pressures, although the activation energy for carrier production diminishes considerably with pressure. Their behavior is entirely reversible. At low temperature ($\sim 78^\circ\text{K}$) for pentacene the activation energy goes to zero above 200 kbar and the material becomes a metal or semimetal. Below 200°K this behavior is reversible. At high pressures and temperatures above 200°K , the resistance tends to drift upward with time and this behavior is irreversible. The material can be recovered in milligram quantities. Ordinary pentacene is a bluish-black crystalline material which sublimes easily at 120°C in a vacuum. Its electronic absorption spectrum shows peaks in the region 14–18 kK. As mentioned above, these relatively low energies are associated with the long conjugation path. Its infrared spectrum in the C–H stretching region shows only typical aromatic frequencies. The high pressure product is reddish brown and amorphous. It will not sublime at 350°C in a vacuum. The low-lying peaks in the electronic spectrum have disappeared, although there are absorptions which correspond to shorter conjugation paths. The infrared spectrum shows, in addition to the aromatic C–H stretch, a second peak of about equal intensity in the region associated with aliphatic C–H stretching vibrations. There are other drastic differences in the infrared spectrum. It seems clear that the pentacene has polymerized, although the small amounts of material and its extreme insolubility make it difficult to characterize the polymer precisely.

A reasonable mechanism is as follows. The shift of the π^* state to lower energy (vis à vis the π ground state) is sufficient that at high pressure the electrons are largely in this more reactive state. (The two states are probably mixed by configuration interaction as shown in Figure 1.) The reaction may