crystals, and that these crystals were relatively free from structural defects. For direct transmission measurements, these crystals were 'freely' mounted using PTFE sheet as a substrate. The thin sheet of PTFE was glued to an aluminium foil. A small slit was cut through the substrate, over which the crystal was attached with the aid of a spot of silicone rubber cement (ICI Silcoset 151). The specimen was finally sealed between two spectrosil discs (not in contact with the crystal). The package was then immersed in either liquid nitrogen or liquid helium for transmission measurements. A gas-exchange dewar was used for measurements taken at intermediate temperatures between fixed points of liquid nitrogen, solid carbon dioxide and ice. The temperature was recorded using a copper–constantan thermocouple.

Specimens for the measurement of pressure coefficients were mounted directly onto the sapphire window of the high pressure cell†. There would be residual strain in the crystal at low temperatures, owing to the difference in the thermal contraction between the crystal and the substrate. However, since measurements were made of the variation of exciton energy with pressure, these should not be affected by the residual strain at equilibrium. Evaporated films were used in the measurement of the pressure dependence of the higher energy exciton peak (5 ev) in TlBr, and in all the measurements on TlCl and TlI. This is due to the fact that, in the case of TlBr, there was a need for a thinner and larger crystal than the ultramicrotome could provide, and in the latter cases, there were no single crystals available. These thin films, varying in thickness between 300 Å and 2000 Å, were evaporated onto the sapphire window at room temperature using powder of 4N8 purity. In order to check the results obtained from evaporated films against those from crystals, a comparison was made of the pressure coefficient for the minimum gap exciton energy in TlBr.

A high pressure system similar to that of Fitchen (1963), which employs helium gas as the pressure transmitting medium, has been constructed. This consists of a two-stage gas compressor which raises the pressure of the He gas from approximately 0·14 kbar from a pressurized cylinder to 2 kbars, followed by an oil pump in conjunction with a gas–oil separator to produce a final pressure of just over 6 kbars. The high pressure optical cell was constructed using beryllium–copper, and sintered sapphire cylinders as optical windows. One of these windows was also used as the substrate for both evaporated films and single crystals. This cell forms the tail end of a cryostat which allows it to be cooled by conduction to near liquid nitrogen temperature ($\sim 80\,^{\circ}\mathrm{K}$). Reproducibility of an exciton peak position in transmission at a given pressure and temperature, when an evaporated film or a single crystal was used, was ensured by cycling the pressure. The consistency was good, provided thermal equilibrium was attained before each measurement.

---

† Similar results for pressure coefficients were obtained with a freely mounted crystal at room temperature.

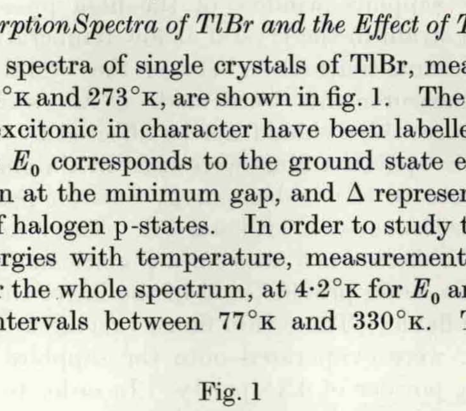
The high resolution optics was provided by either a Barr & Stroud double prism monochromator or a Monospek 1 metre focal length, 1200 lines/in. grating monochromator. The former was used in the measurements of pressure coefficients with a typical resolution of 5 Å, while the latter was used in the measurement of the absorption spectra with a typical resolution of 1 to 2 Å. A 150 w tungsten–halogen and a 40 w deuterium arc lamp provided the visible and ultra-violet radiation, respectively. The specimen was situated after the monochromator. The signal detection system consited of a mechanical chopper for modulating the light intensity, an EMI 9558 Q photomultiplier, a phase-sensitive lock-in amplifier and a chart recorder.

§ 3. Results

3.1. *AbsorptionSpectra of TlBr and the Effect of Temperature*

The absorption spectra of single crystals of TlBr, measured directly in transmission at 78°K and 273°K, are shown in fig. 1. The major absorption peaks which are excitonic in character have been labelled E_0, E_1, $E_1+\Delta$, E_2 and E_3, where E_0 corresponds to the ground state exciton associated with the transition at the minimum gap, and Δ represents the spin–orbit splitting energy of halogen p-states. In order to study the dependence of these exciton energies with temperature, measurements have also been made at 194°K for the whole spectrum, at 4·2°K for E_0 and E_1, in addition to E_0 at 10°K intervals between 77°K and 330°K. These results are

Fig. 1



Absorption spectra of single crystals of TlBr at 78°K and 273°K.