Recently, however, it has been established (Grant *et al.* 1970, Grant and Yoffe 1970, 1971) that pressure coefficients in a number of materials including both cubic and layer crystals (e.g. $TlBr$, PbI_2, As_2Se_3, etc.) do normally increase with increasing temperature. It should be possible to describe the implied temperature dependence of the deformation potential in terms of the pseudopotential model, but there is as yet to our knowledge no detailed theory to account for this effect.

We will then consider the increase in pressure coefficients between $80°K$ and $290°K$ as ' normal ' behaviour, and reserve the previous explanation involving a reduction in the exciton binding energy for the *non*-linear region of pressure shift observed by Connell *et al.* at pressures in excess of 30 kilobars.

4.1.3. *Lattice dilatation and the electron–lattice interaction*

An important reason for measuring the pressure coefficient of interband transitions is to determine how much of the temperature coefficient of the energy of the interband transition in question arises from thermal expansion and how much from the electron–lattice interaction. Since the energy of a transition is a function of the pressure, temperature and volume of the solid, it may readily be shown that

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V - \frac{\alpha}{\beta} \cdot \left(\frac{\partial E}{\partial p}\right)_T, \quad \cdots \cdots \quad (1)$$

where the expansion coefficient $\alpha = 1/V \cdot (\partial V/\partial T)_P$ and the isothermal compressibility $\beta = -1/V \cdot (\partial V/\partial P)_T$.

This equation expresses the temperature coefficient of an energy gap E as the sum of two terms. The first term on the right-hand side relates to the change in energy gap with temperature at constant volume, and is a measure of the electron–lattice interaction, or the degree to which energy levels are perturbed by lattice vibrations. The second term expresses the energy change due to lattice expansion in terms of the expansion coefficient, the isothermal compressibility and the pressure coefficient. Independent measurements of the temperature and pressure coefficients therefore permit an estimate to be made of the electron–lattice interaction, provided that α and β are known.

In these layer crystals the crystallographic c axis is normal to the plane of the layers, and we may take two other equivalent directions as lying in the plane of the layers. To take account of this crystal anisotropy the last term in eqn. (1) is modified (Davies 1970, private communication) to become

$$\left(\frac{\alpha_\parallel + 2\alpha_\perp}{\beta_\parallel + 2\beta_\perp}\right) \cdot \left(\frac{\partial E}{\partial p}\right)_T, \quad \cdots \cdots \quad (2)$$

where the subscripts denote directions parallel $\parallel$ and perpendicular $\perp$ to the c axis. The pressure coefficient refers to hydrostatic pressure, and the compressibilities refer to strains produced by hydrostatic pressure. This expression naturally reduces to the original one for a cubic system.

Flack (1970) has measured $\beta_\parallel$ and $\beta_\perp$ for several layer crystals, and his results are presented in table 3. The compressibility is, as expected, considerably greater parallel to the c axis than in a direction lying parallel to the crystal layers. This effect is to be attributed to the easy reduction under pressure in the van der Waals gap between successive MX_2 sandwiches.

Young (1968) measured the variation with temperature of the lattice parameter in MoS_2 normal to the c axis, using crystals mounted on a cold stage in an electron microscope. The value of $\alpha_\perp$ obtained from his data is $\alpha_\perp = 32 \times 10^{-6}/\mathrm{deg}.$ at $290°\mathrm{K}$.

No direct measurement of $\alpha_\parallel$ for MoS_2 has been found in the literature. Brixner (1963) has however measured $\alpha_\parallel$ and $\alpha_\perp$ for tungsten diselenide WSe_2, which has the same crystal structure as MoS_2. Brixner obtained $\alpha_\parallel = 10\cdot6 \times 10^{-6}/\mathrm{deg}.$, and $\alpha_\perp = 6\cdot8 \times 10^{-6}/\mathrm{deg}.$ The large discrepancy in the above values of $\alpha_\perp$ for MoS_2 and WSe_2 is surprising, but in the absence of a direct measurement, we estimate $\alpha_\parallel$ for MoS_2, using the same ratio between $\alpha_\parallel$ and $\alpha_\perp$ as for WSe_2, to be $\alpha_\parallel = 50 \times 10^{-6}/\mathrm{deg}.$ for MoS_2 at $290°\mathrm{K}$.

The above values of expansion coefficient and compressibility, together with the pressure coefficient of peak A in $2H$–MoS_2 at $293°\mathrm{K}$, lead to a lattice dilatation term of value, $-1\cdot0 \times 10^{-4}$ ev/deg.

The temperature coefficient at room temperature of the A peak in 'freely mounted' crystals of $2H$–MoS_2 (Frindt and Yoffe 1963) can be estimated as $-3\cdot0 \times 10^{-4}$ ev/deg., so that the lattice dilatation accounts for just one-third of the temperature shift of peak A at room temperature. The electron–lattice term is left with the value (from eqn. (1)) $-2\cdot0 \times 10^{-4}$ ev/deg., with the usual negative sign predicted by Fan (1951, 1967).

An estimate may be made of the electron–lattice interaction term at $80°\mathrm{K}$ assuming that the ratio involving expansion coefficients and compressibilities in the expression (2) does not change significantly between $290°\mathrm{K}$ and $80°\mathrm{K}$. The temperature coefficient of peak A at $80°\mathrm{K}$ from Frindt and Yoffe (1963) is approximately $-1\cdot7 \times 10^{-4}$ ev/deg. The pressure coefficient of peak A at $80°\mathrm{K}$ given in table 1 leads to a lattice dilatation term of value $-0\cdot8 \times 10^{-4}$ ev/deg., so that the electron–lattice term must have the value $-0\cdot9 \times 10^{-4}$ ev/deg.

The reduction in magnitude of the electron–lattice term at low temperature is in agreement with Fan's theory of the electron–lattice interaction. Accurate measurements of expansion coefficient and compressibility as functions of temperature are required, however, before weight can be attached to the numerical value of the electron–lattice term at $80°\mathrm{K}$.