of k_2, however, indicates that the second-order term tends to accelerate the softening in ω^2 with pressure.

We find that the magnitude of the force constant ratios S is quite similar for the three optical modes considered and in agreement with the requirement for a homological relationship to exist. The strong decrease of the force constants in progressing from Se to Te, reflected by the average value of $S = 0.63 \pm 0.05$ is also noteworthy.

From the fact that the optical phonons soften slightly when applying pressure, we already know $K_{Se}(40) < K_{Se}(0)$. The small value obtained for S therefore demonstrates the weakening of the intrachain forces with the progression from the lighter (Se) to heavier (Te) element.

6.2 Discussion of the acoustical modes

In calculating the force constant ratios for the long-wavelength acoustical modes we use the equations (10) and (11). Again, owing to the limited pressure range available in the present experiments we only have the linear part in the pressure expansion of v^2. However, due to the remarkably large and positive pressure coefficients found here, the transformation Te → Se cannot always be performed: a linear extrapolation to -35 kbar makes v^2 negative for at least one of the modes in Te. This is, of course, no problem for the transformation Se → Te. The difficulty in Te → Se most likely arises from omission of higher-order pressure effects, which seem to be of particular importance for the long-wavelength acoustical modes. These modes, and especially those with phase velocities in the basal plane, are dominated by the interchain force constants. As discussed previously, and demonstrated in the present experiments, these force constants stiffen very rapidly with pressure. A certain nonlinearity in the pressure behaviour of these modes should be expected from the foregoing discussion of the pressure dependence of the force constants (see Section 4 and also [9]). For the velocities corresponding to wave propagation in the Z-direction, for which the linear Te → Se transformation could be performed, we find reasonable correspondence between the two first-order estimates of the force constant ratios S_1 (see Table 5), again indicating the reciprocity in S for the two transformations. Assuming that we always can use the condition $S = = S_2 = S_{B \to A} = S_{A \to B}^{-1}$, we can again expand v^2 to second order in pressure with the approximation $k_2 = k_2^{Te} = k_2^{Se}$; and find simultaneous solutions for S_2 and k_2. As for the optical modes, we expect S_2 to be a best average estimate of the force constant ratio S.

From the data in Table 5 we make the following observations: (i) The sign of the predicted second order pressure coefficient k_2 in v^2 is always positive, i.e., the stiffening of the acoustical modes is accelerated by the inclusion of the second-order pressure term. We recall that for the optical frequencies the softening was found to accelerate. These findings are consistent with the pressure dependence of the respective force constants as discussed in Section 4. (ii) The values of S_2 for all the acoustical modes considered are quite similar, about 0.52 ± 0.09. This agrees quite well with the value range found for S_2 in the optical modes (Table 4). This is a particularly important result because it shows that the vibrational modes in Se(p_{Se}) and Te(0) or equivalently in Se(0) and Te(p_{Te}) can be related to each other by a single universal scaling factor! We recall that this is a necessary condition for a homological relationship to exist between the vibrations in the two species (via their respective pressure be-
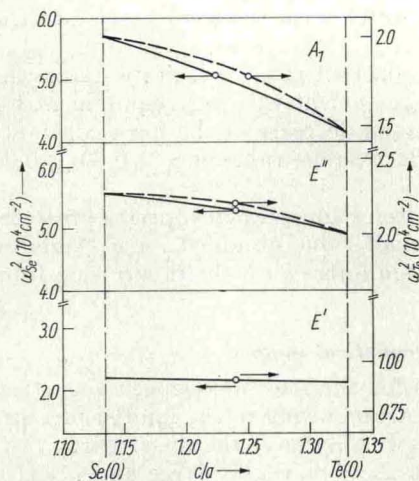
37*

Fig. 3. Comparison of the c/a-dependence of ω^2 for the optical modes in Se and Te
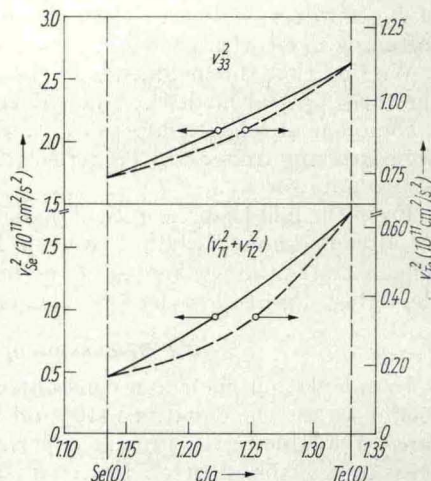
Fig. 4. Comparison of the c/a-dependence of v^2 for two acoustical modes in Se and Te

haviours). But again, although this study covers only a limited set of phonons at the zone centre, a wide range of atomic inter- and intrachain force constants are nonetheless involved. To complete the study, therefore, one needs information about the pressure behaviour of additional phonons, for instance, at the zone edge; an experimental undertaking that most probably will have to involve neutron spectroscopy.

In the diamond type materials the mode force constant ratio is given by [12]: $S_{B \to A} = a_B^3/a_A^3 = V_B/V_A$, where a and V are lattice constant and volume of the unit cell for materials A and B, respectively. Calculating now this volume ratio for $A = Te(0)$ and $B = Se(40)$ we obtain the value $S_{B \to A} = 0.624$. This number is quite close to the values listed for S in Tables 4 and 5. It demonstrates that the force constants in this case seem to be also mainly governed by a simple $1/V$ behaviour as was found in the diamond family [12].

Finally, in Fig. 3 and 4, we present a comparison of the c/a-dependence of some optical and acoustical modes in Se and Te, based on the various pressure dependences discussed earlier. For clarity the curves of ω^2 and v^2 have been scaled by the individual force constant ratios S $(= S_2)$ as given in Tables 4 and 5. This makes the end points of the corresponding Se and Te curves coincide, per definition. For the optical modes the largest mismatch between the Se and Te curves is about 4% in the case of ω_{A1}^2. The mismatch for the acoustical modes is 5% for v_{33}^2, and as much as 20% for $v_{11}^2 + v_{12}^2$. The latter, corresponding to a radial compression in the basal plane, also has the most "anomalous" force constant ratio S (i.e. the largest deviation from the average value of S). This shows therefore that of the vibrational modes investigated, this particular mode has the poorest compliance with the scaling laws of the Se–Te homology.

7. Conclusion

We have presented a study of the pressure coefficients of various zone centre vibrational modes in Se and Te.