

In figure 13 we give a comparison of the experimental value of  $U_z$  with the calculations of London (1954); it can be seen that the volume dependence of  $U_z$  is reasonably well reproduced by this theoretical expression. It must, however, be borne in mind that the uncertainty in the experimental value of  $U_z$  is large, mainly because of uncertainties in the interatomic potential used to calculate  $\Phi$ . By comparing the de Boer–Michels potential with other proposed potentials (Yntema & Schneider 1950; Slater & Kirkwood 1931) one finds that uncertainties of up to 15% exist due to this cause. Therefore the rather good agreement of London's calculations with the experimental results is partly fortuitous.

A different approach to the calculation of the zero-point energy is through the vibrational properties of the lattice. Domb & Salter (1952) showed that at least for cubic Bravais lattices and harmonic oscillations the zero-point energy is given very closely by

$$U_z = \frac{9}{8}R\theta_\infty, \quad (18)$$

where  $\theta_\infty$  is the (theoretical) high-temperature limit of the Debye temperature. Salter (1954) has used this expression for the discussion of the zero-point properties of the heavier rare gas solids. No satisfactory theoretical derivation of equation (18) has been given for the case of helium where the zero-point vibrations are strongly anharmonic. Nevertheless, our results on helium show that  $U_z$  is proportional to  $\theta_D$  for both isotopes ( $\theta_D$  is again evaluated at the same reduced temperature for all densities in both isotopes). They show further that the constant of proportionality is about that to be expected from equation (18) if one estimates  $\theta_\infty$  from the low-temperature part of the curve of  $\theta_D$  against  $T$ . It is thus probable from the evidence of the present experiments that even in this extreme case, equation (18) still describes the experimental results surprisingly well.

Although the large amplitude of the zero-point motion in solid helium introduces many difficulties into the calculation of  $U_0$  at low densities, it is to be expected that as the density increases (volume decreases) the zero-point energy will become less and less important in comparison with the energy associated with the repulsive forces between the atoms. ( $U_z$  varies approximately as  $V^{-2}$  (since  $\gamma \simeq 2$ ) whereas the potential of the repulsive forces varies as something like  $V^{-4}$ .) At small enough volumes, therefore, we may expect that the ratio of the values of  $U_0$  for both isotopes will tend towards unity. Similarly, the restoring forces produced when the lattice is perturbed will tend to become the same in the two isotopes so that the frequencies of the resulting vibrations will be determined by the ratio of the masses of the two kinds of atoms, i.e. the ratio  $\theta_3/\theta_4$  will tend to the limiting value  $(m_4/m_3)^{\frac{1}{2}}$  as the volume is diminished, provided that no changes in the electronic band structure of the solids intervene.

In table 13 we give the ratio of the Debye temperatures for  $^3\text{He}$  and  $^4\text{He}$ , compared at the same molar volume and at the same reduced temperature, in units of  $(m_4/m_3)^{\frac{1}{2}}$ . The ratio of the Debye  $\theta$ 's measured at the same reduced temperature varies very little with temperature so that this comparison can be made quite accurately. It can be seen that the ratio of the Debye temperatures tends towards  $(m_4/m_3)^{\frac{1}{2}}$  at low molar volumes. At high molar volumes, this ratio is exceeded by up to 7%. This is qualitatively in accordance with perturbation anharmonic theory which shows that when anharmonic effects come in, the  $\theta$  of the lighter isotope (in which therefore the anharmonic effects are greater) will increase more rapidly than that of the heavier isotope (T. H. K. Barron, private communication).