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It will be noticed that the theoretical absorption bands are considerably sharper than those actually observed. This is probably due to the fact that in the theory we are dealing with ideal spherical particles all of the same size, while in practice deviations from ideal conditions will almost certainly take place. However, the general agreement is fairly good, and the theory suggests that the particle size is of the order of 100 Å.

When a crystal which has been partially decomposed with ultra-violet light only is irradiated with infra-red light for 2 hours, the absorption band in spectrum A shifts from 4000 Å to about 5200 Å. The absorption band in spectrum B, however, is not significantly altered. After this treatment the crystal is strongly dichroic. Rogers and Sawkill (unpublished work) obtained a similar result by irradiating an undecomposed crystal with the full output of the mercury lamp.

If the heating effect of the infra-red light causes coagulation of the silver nuclei, we should expect the absorption band to shift to longer wavelengths in both spectra. It is not understood why this is not observed. A shape effect may be operating.

An electron microscope study of the physical changes taking place during the decomposition of a number of metallic azides is being made at present, and it is hoped that this will give more information regarding the shape and size of the metallic nuclei.

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Melting Curves of Helium and Hydrogen Isotopes

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MILLS AND GRILLY (1955) have recently determined the melting curves of ^{4}He and ^{3}He over a considerable pressure range. For ^{4}He their results agreed with previous measurements of Simon and his collaborators (Holland *et al.* 1951, Dugdale and Simon 1953) and on fitting the data to a Simon melting curve

$$P = \alpha + \beta T^c, \qquad \ldots\ldots(1)$$

the value of α is negative, corresponding to a positive 'internal pressure'. For ^{3}He, on the other hand, the value of α is positive and this corresponds to a negative internal pressure. It is of interest to see how this result fits in with the theoretical treatment of solid helium.

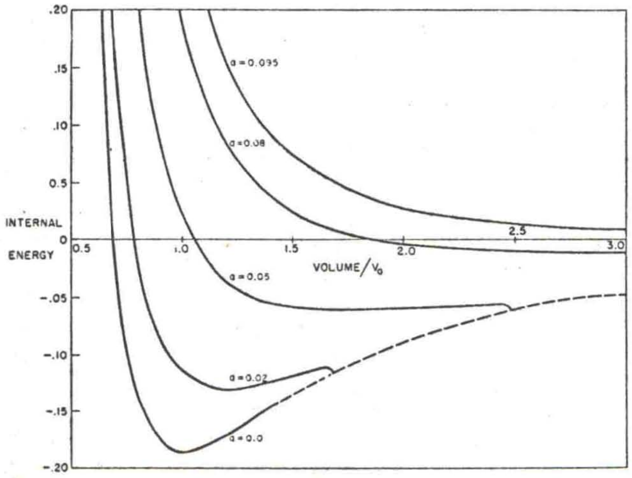
In an attempt to account for the properties of substances in which the role of zero-point energy is important, the present writer put forward the following differential equation for the Debye Θ value (Domb 1952):

$$\Theta = 0{\cdot}4109\,\frac{h}{k}\left[\frac{\phi''(r)}{m} + \frac{9}{8}\frac{R}{m}\frac{d^2\Theta}{dr^2}\right]^{1/2} \qquad \ldots\ldots(2)$$

where $\phi(r)$ is the lattice energy per particle, and m the mass of the particles. This equation was rewritten by Dugdale and MacDonald (1954) as an equation for the internal energy at absolute zero E_0 in the form

$$E_0 = \phi(r) + a\left(\frac{d^2E_0}{dr^2}\right)^{1/2} \qquad \ldots\ldots(3)$$

where a is a constant inversely proportional to $m^{1/2}$ which represents the effect of zero-point energy. Dugdale and MacDonald put forward an approximate solution in closed form when $\phi(r)$ is a Mie–Lennard-Jones 6–10 potential, and this solution has a number of interesting physical properties.



The internal energy E_0 at absolute zero plotted as a function of volume, for various values of a (see equation (3)).

The form of E_0 as a function of volume for varying a is shown in the figure. As a increases the minimum is pushed out and the potential well becomes shallower until, for a particular critical value a_c, E_0 ceases to have a minimum. It seems that ^{4}He with a positive internal pressure corresponds to a value of $a < a_c$, whereas ^{3}He corresponds to $a > a_c$. For ^{4}He the solid phase could exist under atmospheric pressure, but the liquid phase is more stable; for ^{3}He, however, the solid phase could not exist.

The accuracy of the solution of Dugdale and MacDonald in the region of applicability to ^{4}He and ^{3}He, and the dependence of the solution on the form of intermolecular potential are being investigated by M. E. Fisher and I. J. Zucker at King's College.

By means of measurements of the Debye Θ-values of ^{4}He along the melting curve Dugdale and Simon (1953) were able to show that the degree of degeneracy steadily increased as the melting temperatures and pressures increased, and there are also theoretical reasons for expecting this type of behaviour (Salter 1954). One might, therefore, expect that sufficiently far along the melting curve classical theory is valid, and the curves for ^{4}He and ^{3}He become identical. It is difficult to assess how much reliance can be placed on extrapolations based on the formulae of Mills and Grilly (1955), but it is interesting to note that despite the initial apparent parallelism of the melting curves, these formulae do lead to an intersection at a temperature of 55° and a pressure of 9000 atmospheres.

For the hydrogen isotopes H_2, D_2 and T_2 the structure of the molecule is to some extent dependent on the isotopic mass, and it is, therefore, no longer rigorously true to say that in the region where melting is classical the melting curves would be identical (except at much higher pressures where the substance becomes monatomic). Nevertheless, it is worth pointing out that despite the initial parallelism noted by Chester and Dugdale (1954) subsequent measurements by Mills and Grilly (1956) indicate that the melting curves are approaching one another at higher temperatures and pressures.

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