Lattice Defects and the Self-Diffusion and Anomalous Specific Heat in Solid α-He³†

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By using a simple model for lattice defects we have tested the hypothesis that the anomalous specific heat and the self-diffusion in solid α-He³ are the result of the formation of lattice defects. It is found that vacancies and interstitials are present in about equal numbers and that their formation, probably in pairs, gives rise to the observed specific heat anomaly. It is contended that the motion of the vacancies gives rise to the self-diffusion.

SELF-DIFFUSION in solid α-He³ has been observed by Goodkind and Fairbank[1] and by Reich[2] using nuclear spin relaxation techniques. The diffusion constant D was found to obey the familiar relation

$$D = D_0 e^{-W/kT}, \qquad (1)$$

and the activation energy for self-diffusion, W, was determined at a number of densities.

A low-temperature anomalous contribution to the specific heat of solid α-He³ has been reported by Heltemes and Swenson.[3] The deviations from the Debye contribution could be fitted by an "Einstein" or "Schottky" expression of the form

$$C_v/R = 2(\varphi/T)^2 e^{-\varphi/T}. \qquad (2)$$

This result has recently been confirmed by measurements of Edwards, McWilliams, and Daunt.[4] These authors draw attention to the rather close agreement between the activation energy for self-diffusion, W/k, and the energies φ of (2), both as functions of the density. They suggest that both phenomena may result from the formation of vacancies. The same suggestion has been forwarded by Reich.[5]

By using a simple model for defect formation we have tested the hypothesis that formation of lattice defects gives rise to the anomalous specific heat. We arrive at the conclusion that vacancies and interstitials are formed in about equal numbers (either separately or in pairs) but that it is probably the motion of the vacancies that gives rise to the self-diffusion. However, to account in detail for the diffusion data, the diffusion mechanism has to be studied more carefully.

The fact that both vacancies and interstitials are formed is a direct consequence of the fact that both defects require about the same energy for their formation. According to the simple theory of lattice defects[6] it should, in principle, be possible to decide from the form of the specific heat whether vacancies and interstitials are created individually or in pairs (Frenkel defects). In both cases the specific heat is of the form

$$C_v/R = C(W/kT)^2 e^{-W/kT}. \qquad (3)$$

W is the formation energy of either vacancy or interstitial (which are found to be equal), and consequently half the formation energy of a pair. In the case of independent formation $C = 1 + \alpha$, while for pair formation $C = 2\sqrt{\alpha}$, where α is the number of interstitial positions per lattice site. For the bcc lattice $\alpha = 3$, and hence $C = 4$ for independent formation and $C = 3.5$ for pair formation ($C = 1$ if only vacancies are formed). Both numbers are fairly close to the experimental value $C = 2$ appearing in (2). In fact, if reliable, this comparison points to the formation of pairs. This is what one would expect, considering the fact that pairs can be formed at constant volume (blocked capillary technique) without requiring a density change in the system. However, neither theory nor experiment are sufficiently accurate to decide between the two mechanisms.[7]

The model which was used is the following: A vacancy is pictured as a small region in the crystal where the density is slightly lower than average, i.e., we assume that a small number of atoms n_v equally share the vacancy volume. Similarly, the interstitial is considered as a small region of slightly higher density, where n_i atoms equally contribute to provide the volume for the intruding atom. The total volume remains unchanged. The formation energies of these defects can be expressed in terms of the total lattice energy E. One finds for the formation energy W_F of a Frenkel defect of this type (which is the sum of the vacancy formation energy

¹ J. Goodkind and W. M. Fairbank, Phys. Rev. Letters 4, 458 (1960) and in *Helium Three*, edited by J. G. Daunt (Ohio State University Press, Columbus, Ohio, 1960), p. 52.
² H. A. Reich, in *Helium Three*, edited by J. G. Daunt (Ohio State University Press, Columbus, Ohio, 1960), p. 63.
³ E. C. Heltemes and C. A. Swenson, Phys. Rev. Letters 7, 363 (1961).
⁴ D. O. Edwards, A. S. McWilliams, and J. G. Daunt, Phys. Letters 1, 218 (1962).
⁵ See E. C. Heltemes and C. A. Swenson, Phys. Rev. 128, 1512 (1962).

⁶ See, for instance, A. Seeger, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7, Part I, p. 383.
⁷ There seems to be some uncertainty in the factor 2 appearing in (2). From our own evaluation of Heltemes and Swenson's data (reference 5) we find values for the factor in (2) varying between 1.5 and 4.6.

W_v and the interstitial formation energy W_i)

$$W_F = W_v + W_i = \frac{1}{2}\left(\frac{1}{n_v} + \frac{1}{n_i}\right)\frac{V^2}{N}\left(\frac{\partial^2 E}{\partial V^2}\right)_T. \quad (4)$$

V is the molar volume, N is Avogadro's number, and E is the total lattice energy per mole. In the temperature range of interest one has $V(\partial^2 E/\partial V^2)_T \approx 1/\beta$, where β is the isothermal compressibility. For the formation energy of any one of these defects we may thus write

$$W(V) \approx V/KN\beta(V), \quad (5)$$

where K is a constant determined by n_v and/or n_i, depending on the type of defect.

It should be noted that the total lattice energy is used in the evaluation of the defect formation energies, so that the local changes in the zero-point energy, which are apt to be important, are automatically included.

For Frenkel defects, φ in Eq. (2) should be equal to $W_F/2k$, whereas for vacancies alone, φ would be W_v/k. But $W_v \approx \frac{1}{2}W_F$, since n_v and n_i are almost equal ($n_v = 8$, $n_i = 7$ if nearest neighbors of the defects participate in the regions of lower and higher density). Therefore, from the magnitude of $\varphi(V)$ alone we cannot decide whether Frenkel defects (pairs) or vacancies are formed.

By evaluating (5) as a function of V we can check whether the calculated formation energies W exhibit the correct density dependence. We have used the experimental values of β plotted by Heltemes and Swenson.[5] The calculated values of W can be made to agree closely with the experimental ones by choosing $K = 8.22$ in (5) (cf. Fig. 1). This means that about four atoms participate in both the vacancy and the interstitial. This is of the right magnitude and lends support to the model.

Edwards, McWilliams, and Daunt[4] consider the values of the activation volume $R(d\varphi/dp)$ to indicate that vacancies are formed. However, for experiments performed at constant volume it is more appropriate to consider the activation pressure. From Heltemes and Swenson's data one finds $-\frac{1}{2}R(d\varphi/dV) = 77$ atm. This means that the creation of $\frac{1}{2}$ mole of defects (per mole of substance) raises the pressure by only 77 atm. If the
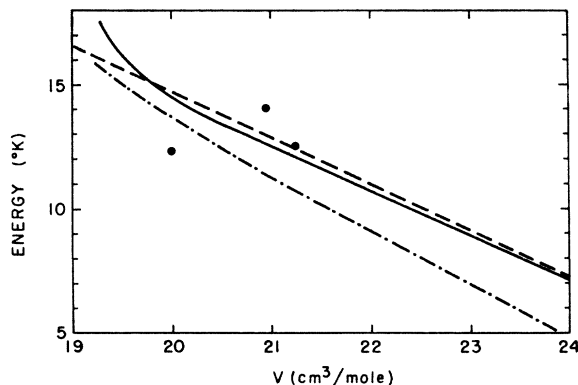

FIG. 1. Activation energies as functions of V. Solid line, W/k, calculated from (5) with $K = 8.22$; solid circles, W/k, Goodkind and Fairbank[1]; dash-dotted line, W/k, Reich[2]; dashed line, φ, Heltemes and Swenson.[3]

defects were vacancies, the creation of $\frac{1}{2}$ mole of them would reduce the volume occupied by the system by $\frac{1}{3}$ or $\frac{1}{2}$. This would show up in a very much larger pressure increase. This, again, supports the conclusion that the defects are both vacancies and interstitials.

To account for the self-diffusion data the diffusion mechanism has to be considered in detail. At present, we can only say the following. In Eq. (1) W is the sum of the formation energy of the defect, giving rise to the diffusion, and the activation energy for hopping motion. Offhand one expects vacancies to move more easily than interstitials. Further, since the bcc lattice of He^3 is a rather open structure, one expects the activation energy for vacancy hopping to be essentially smaller than the formation energy for vacancies. Under these assumptions $W[\text{Eq. (1)}] \approx W_v$ and this would account for the close agreement between W/k and φ, which is found experimentally.