Formation of Nonlocalized Vacancies in bcc He^3 *

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Several experiments have indicated the formation of some defect in body-centered cubic solid He^3 at relatively low energies. A few alternative hypotheses are discussed which could explain this effect, but vacancy formation is singled out for study. The wave function and formation energy of vacancies in solid He^3 are then calculated variationally, and it is found that such a vacancy would be highly nonlocalized and would propagate as a wave in the crystal. The calculation of the energy of formation, actually an energy band, uses the Nosanow cluster expansion. The energy so calculated is compared with the experimental formation energies, and it has the correct dependence on density although it is higher than the experimental values.

I. INTRODUCTION

Several experiments on solid He^3 lead to the conclusion that in the bcc phase some mechanism can be excited thermally. For example, Heltemes and Swenson[1] and Edwards *et al.*[2] found an exponential contribution to the specific heat in this phase of solid He^3. This early work was followed by the work of Sample and Swenson[3] and Pandorf and Edwards.[4] These experiments are in excellent agreement on the specific heat of solid He^3, and Sample and Swenson have calculated a density-dependent formation energy from their measured specific heats. The thermal-conductivity experiments of Bertman *et. al.*[5] can be interpreted as indicating the formation of some entity which scatters phonons in order to explain an exponential part in the thermal resistance. Bertman *et al.* assumed some defect formation and calculated an exponential coefficient which can be interpreted as a formation energy. Finally the thermal self-diffusion rate as determined by nuclear magnetic resonance in bcc He^3 by Reich[6] indicates a diffusion activation energy in agreement with the above two experiments. The results of these three types of experiments are the experimental points in Fig. 2. Taken together they give strong evidence for the formation of some "defect" in the He^3 lattice.

The most frequent proposal as to the nature of this "defect" has been that the entities excited in He^3 are vacancies. This possibility along with the possibility of them being interstitials was mentioned by the authors of the earliest experiments.[1,2] Other suggestions for the identity of this effect are the Frenkel pair (a vacancy and interstitial not associated with one another) and the vacancy-interstitial bound state. In the latter case it has been argued that an atom could become dislodged from its lattice site, but might be attracted to the neighborhood of the vacant site perhaps because of the lower density in the neighborhood.

In favor of the interstitial atom hypothesis is the fact that when an atom moves from the surface to an interstitial site a substantial reduction in energy occurs due to the reduction in volume of the crystal in the presence of external pressure. In vacancy formation the same energy must be added into the energy of formation. On the other hand, this energy increases in magnitude as the pressure is increased and since the experimental energy does likewise the vacancy would be favored. Furthermore we do not believe that an interstitial could have the low energy required by the experiments since we believe it would have to strongly distort the lattice so as to involve 30–50 neighbors to lower the kinetic energy of the interstitial atom sufficiently. If valid, this last objection also holds against the Frenkel pair. It also holds against the vacancy-interstitial bound state unless the interstitial is very much localized in its original lattice site. In this case, however, it is expected that the entity would be similar to a He^3 atom in the second excited state of its Hartree well. Such a state has been used[7] to calculate the phonon spectrum via random phase approximation and could therefore be represented by a linear combination of phonon states. Such a state could only be the entity we seek if distortion of the lattice about the excited atom lowered its energy strongly. In the phonon picture this would be represented by a strong curving of the phonon spectrum. A higher random-phase-approximation calculation not reported here has not indicated such a distortion of the phonon spectrum.

Therefore we believe that the most likely indication of the experiments is that vacancy formation takes place in bcc solid He^3. We cannot rule out the possibility that the actual mechanism is interstitial formation or some more exotic effect. It is in the light of these considerations, however, that we have been motivated to study the vacancy in solid He^3. We feel that the calculation presented in this paper lends credence to the vacancy picture.

To calculate the vacancy energy one must first have a theory of the ground state. The work of Nosanow *et al.*[8,9] has been used as the primary starting point for this vacancy-energy calculation. The effects of phonons[10] and cubic symmetry[11] are omitted from Nosanow's formulation, however, their effect on the ground-state energy is small and would presumably be small for the vacancy calculation also. Probably the most severe difficulty with the Nosanow theory is the use of a cluster expansion for the evaluation of the integrals $\langle\Psi|H|\Psi\rangle$ and $\langle\Psi|\Psi\rangle$. Using Monte Carlo tech-

niques Hansen and Levesque[12] have obtained substantially lower energies for the ground-state He^3 system. This is because the cluster expansion of Nosanow does not converge well unless the class of variational functions is limited. Hansen and Levesque were able to go outside of that trial set for which the cluster expansion converges and obtained a ground-state energy in much closer agreement with experiment than workers using cluster expansions.[13] The difference between the Hansen-Levesque wave function and the Nosanow wave function is significant enough to change our results; the advantage of the cluster-expansion method is the great speed with which the computations can be done on the computer as compared with the very long times necessary for a Monte Carlo calculation.

In calculating the vacancy formation energy in solid He^3, we have first calculated the energy to form the vacancy in the cluster-expansion approximation without any deformation of the crystal. A principal contribution is the energy PV_0 necessary to expand the crystal against the external pressure. The crystal is assumed to expand by one atomic volume, V_0, for each vacancy formed.[14] Next, the energy to move one atom from the interior to the surface must be added. Since a typical surface atom will have just half the neighbors of an interior atom, we need only add the energy to break half the "bonds" between the atom being moved and its neighbors. This energy, of an undistorted vacancy, can easily be obtained from Nosanow.[8] The major part of the calculation then remains; it is to find the effects of distortion of the solid about the site of the vacancy and the effects of vacancy "jumping" on its energy. The latter effect so far as we know is not important in any other solid. In solid He^3, however, the "jumping" of the vacancy is so rapid that the actual wave function of a crystal with a vacancy must be considered to be a linear combination of wave functions each with a vacancy localized on a different site. This results in a band of energies for the vacancy with the energy of a particular state depending on vacancy "momentum" and on the spin configuration of the solid.

We imagine such vacancies to be quite nonlocalized and to propagate in the crystal as waves. Presumably such an entity could diffuse from the edge, where it is probably formed, to the center of a large single crystal as the solid is heated. Thus the question of maintaining thermal equilibrium during formation should not arise as it might for localized vacancies in a large single crystal.

II. THEORY OF THE NONLOCALIZED VACANCY

In view of the small effect on the results of Nosanow when the three-body cluster terms are included[9] and in view of the deficiencies of the cluster-expansion method in general as indicated by the work of Hansen and Levesque, no three-body cluster terms have been included in the present calculation and we have taken consistently the results of Nosanow[8] as the starting point for this calculation.

We assume that the wave function for the crystal containing a vacancy can be written in the form

$$\Psi = \sum_{iS} \alpha_{iS} \Psi_{iS}, \tag{1}$$

where Ψ_{iS} is the wave function for a crystal with a vacancy localized on the site i with spin configuration $S = \{S_1, S_2, \ldots, S_N\}$. Here $S_1, S_2, \ldots, S_N$ are the z components of spin associated with each lattice site. Ψ_{iS} is an antisymmetrized state with the spin on each site specified:

$$\Psi_{iS} = \frac{1}{\sqrt{N!}} \left[\sum_P (-1)^p \prod_j \phi_j^{\,i}(\vec{r}_j)\chi(S_j, \beta_j)\right] \times \prod_{k<l} f(r_{kl}), \tag{2}$$

where $\phi_j^{\,i}(\vec{r}_j)$ is the space single-particle wave function at site j with a vacant site at i, and $\chi(S_j, \beta_j)$ is the spin single-particle wave function with spin component S_j. Here $\vec{r}_j$ denotes the space coordinate of particle j, and β_j denotes the spin coordinate of particle j. The sum over P permutes the particle coordinates relative to the single-particle wave functions. The function $f(r_{kl})$ introduces short-range pair correlations. We will use the same form for f as in Nosanow, although that form will not be fixed in this section. r_{kl} is the magnitude of the difference of the space parts of $\vec{r}_k$ and $\vec{r}_l$, i.e., $r_{kl} = |\vec{r}_k - \vec{r}_l|$. N is the number of particles in the system. When not otherwise indicated products and sums over particle indices will run over all N particles. We will assume that $\phi_j^{\,i}(\vec{r}_j)$ depends on the site j and the location of the vacancy i. In particular, we will assume $\phi_j^{\,i}$, for j first or second neighbors of the vacant site i, to be distorted in shape and moved relative to the normal single particle ϕ determined by Nosanow. Since a wave function for a crystal with a vacancy is orthogonal to the ground-state crystal wave function, we may use the variational method to examine various vacancy wave functions to determine an upper limit for the vacancy energy. If we take as a variational form Ψ defined in (1), where the variational parameters are the α's as well as the variational parameters contained in Ψ_{iS}, we may use the lowest-energy eigenvalue of

$$E \sum_{jT} \langle \Psi_{iS} | \Psi_{jT} \rangle \alpha_{jT} = \sum_{jT} \langle \Psi_{iS} | H | \Psi_{jT} \rangle \alpha_{jT} \tag{3}$$

as an upper limit on the lowest vacancy energy. If we are somewhat less cautious, we may assume that the distribution of eigenvalues in (3) represents the distribution of energy levels in the band of vacancy energies provided the variational parameters in Ψ_{iS} are varied to minimize each eigenvalue independently. This will be true if the vacancy wave function can be written in the form (1) and if only first-neighbor jumps of the vacancy can occur (i.e., if

$\langle \Psi_{iS} | H | \Psi_{jT} \rangle$ is nonzero only for i, j nearest neighbors or if $i = j$), if H does not depend on the spin configuration, and if exchange integrals are neglected. In this case the matrix form (3) is dependent only on kinematic effects as will be seen below. Since exchange integrals are very small we can assume that they are zero. We also assume that the Ψ_{iS} are orthogonal unless they represent vacancies on nearest-neighbor sites, and we assume $\langle \Psi_{iS} | H | \Psi_{jT} \rangle$ is zero unless $i = j$, $S = T$, or if i and j are nearest neighbors with spins the same for corresponding sites in S and T. Therefore the matrix problem in (3) has the following properties: (i) it is of very large dimension M having, for the case of total z component of spin zero,

$$M = (N+1)N!/[(N/2)!]^2$$

elements in a row or column. (ii) The matrix on either the right or left side of (3) has one diagonal element in each row and column plus eight other nonzero elements in each row and column because there are only eight nearest neighbors in the bcc lattice. Except for the signs which might differ because of the antisymmetric products in Ψ_{iS}, all of the off diagonal elements are equal.

We wish to define two numbering systems for the lattice sites in the bcc lattice with vacancy. System I has one of the two interpenetrating simple cubic lattices which form the bcc lattice numbered with even numbers while the other is numbered with odd numbers. System II is defined so as to be convenient when describing two states each with a localized vacancy, the vacancy sites being nearest neighbors in the lattice. For system II we number the occupied one of the two vacancy sites 1 and then proceed numbering the remainder of the sites in any order. Referring to numbering system I, we assume that the sign of each Ψ_{iS} is determined so that the term in Ψ_{iS}, which has the ϕj^i in numerical order in j skipping the ith site and has the $\vec{r}_j$ in numerical order, will be positive. Then if i and j are nearest neighbors and if S and T are such that the spin overlap is nonzero (i.e., unity),

$$\langle \Psi_{iS} | \Psi_{jT} \rangle = (-1)^{i-j+1} \langle 1 | 2 \rangle$$

and

$$\langle \Psi_{iS} | H | \Psi_{jT} \rangle = (-1)^{i-j+1} \langle 1 | H | 2 \rangle$$

where i and j refer to numbering system I. Here

$$|1\rangle = \prod_l \phi_l{}^1(\vec{r}_l) \prod_{k<m} f(r_{km}) \qquad (4)$$

and

$$|2\rangle = \prod_l \phi_l{}^2(\vec{r}_l) \prod_{k<m} f(r_{km}), \qquad (5)$$

where numbering system II is used. The superscript 1 or 2 on ϕ indicates which of the two arbitrary nearest-neighbor sites is vacant. But only nearest-neighbor jumps can occur, and since $i - j$ = odd for such jumps because of the way the lattice is numbered in system I all the signs of the off-diagonal elements in (3) are the same.

We will now introduce a short notation for the large matrices in (3). Since only two different values of matrix element occur the matrix $\langle \Psi_{iS} | \Psi_{jT} \rangle$ will be denoted by (N_0, N_1) and the matrix $\langle \Psi_{iS} | H | \Psi_{jT} \rangle$ will be denoted by (H_0, H_1), where the first term in the parenthesis gives the value of a diagonal element and the second gives the value of one of the nonzero off-diagonal elements. Thus $N_0 = \langle 1 | 1 \rangle$ and $N_1 = \langle 1 | 2 \rangle$. Similarly $H_0 = \langle 1 | H | 1 \rangle$, $H_1 = \langle 1 | H | 2 \rangle$. The eigenvalues of (3) are given by

$$\det(H_0 - EN_0, H_1 - N_1 E) = 0 .$$

If this expression is divided by $(H_1 - N_1 E)^M$, where M is the dimension of the matrix, it becomes

$$\det[(H_0 - EN_0)/(H_1 - EN_1), 1] = 0 .$$

Defining

$$X \equiv -(H_0 - EN_0)/(H_1 - EN_1)$$

this last expression may be written

$$\det(-X, 1) = 0 .$$

The values of X satisfying this expression are just the eigenvalues of the matrix $(0, 1)$. The following observations can be made about the eigenvalues of this matrix: (i) The maximum eigenvalue is 8. (ii) The nth moment of the eigenvalues

$$\mu_n = \sum_{i=1}^{M} (X_i)^n$$

is given by the trace of the matrix $(0, 1)^n$. (iii) If a graph is constructed with a vertex for each row or column and a line corresponding to each off-diagonal element in $(0, 1)$, then the ith diagonal element of $(0, 1)^n$ is just the number of ways of returning to the ith vertex via n steps on the graph. (iv) Since we have allowed only nearest-neighbor jumps it is not possible to return to the same state by an odd number of steps so that all odd moments of the eigenvalues of $(0, 1)$ are zero. Thus the eigenvalues X are symmetrically distributed about zero, and the smallest value for X must be -8. (v) Counting the average number of ways for a vacancy to return to the starting state, assuming spins equally likely to be up as down, we find $\mu_0 = M$, $\mu_2 = 8M$, $\mu_4 = 144M$, and $\mu_6 = 3359M$.

Thus a sixth-degree least-squares polynomial expansion of the distribution of the eigenvalues between 8 and -8 can be obtained. The distribution is shown in Fig. 1. The result will be somewhat different for bcc He^4 because of the symmetric wave function and will also be different for

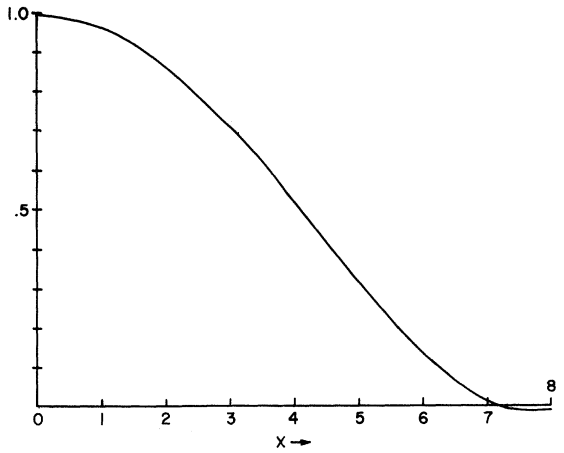

FIG. 1. The distribution of the eigenvalues X, based on a sixth-degree least-squares fit. The distribution is symmetric about X=0 and the maximum eigenvalue is 8.

hcp He^3 or He^4. In the case of hcp He^3, all of the signs of the elements cannot be made the same. Nor is there symmetry of the eigenvalues in either hcp lattice since odd moments can occur.

Solving for E in the definition of X we have

$$E=(H_0+H_1X)/(N_0+N_1X)\ .$$

Since $E_L\equiv H_0/N_0$ is the expectation value for the Hamiltonian for one of the localized vacancies, the reduction in energy from the energy of the localized vacancy state can be written

$$\Delta_1\equiv E-E_L=\frac{(H_1/N_1-H_0/N_0)(N_1/N_0)X}{[1+(N_1/N_0)X]}\ . \quad (6)$$

Here the difference $H_1/N_1-H_0/N_0$ appears explicitly so that cancellations between terms may be taken into account. Similarly the difference in energy Δ_2 between the localized (distorted) vacancy and the undistorted vacancy energy E_u is

$$\Delta_2\equiv E_L-E_u=H_0/N_0-H_0'/N_0'\ , \quad (7)$$

where H_0' and N_0' are defined in the same way as H_0 and N_0 but using the undistorted wave function with one particle removed. For example $H_0'=\langle 1'|H|1'\rangle$, where $|1'\rangle$ is the same as $|1\rangle$ defined in Eq. (4) but with all ϕ's as determined by Nosanow. The undistorted vacancy energy E_u is evaluated in the next section. Finally we may write

$$E=\Delta_1+\Delta_2+E_u\ . \quad (8)$$

III. THE LOCALIZED VACANCY

In this section evaluation of Δ_2 (Eq. 7) and E_u will be considered while evaluation of Δ_1 (Eq. 6) will be discussed in Sec. IV.

The wave function for the localized vacancy is just $|1\rangle$ given by Eq. (4). The form for f is taken from Nosanow

$$f(r)=\exp\{-K[(\sigma/r)^{12}-(\sigma/r)^6]\};$$

here K is a variational parameter in the calculation of the ground-state energy which we take to be the same as in Nosanow, and σ is the parameter in the interparticle potential [see Eq. (15) below]. For those $\phi_j{}^1(\vec{r}_j)$ for any j not first or second neighbors of the vacancy site we have also used Nosanow's form

$$\phi_j{}^1(\vec{r})=\exp[-\tfrac{1}{2}A(\vec{r}-\vec{R}_j)^2]\ . \quad (9)$$

For lattice sites which are first and second neighbors of the vacancy ϕ is allowed to be an elongated Gaussian with the elongation in the direction toward the vacant lattice site, and the center of this elongated Gaussian is allowed to move toward or away from the vacant site. The form is

$$\phi_j{}^1(\vec{r})=\exp[-\tfrac{1}{2}B_j(r_x-R_x+d_j)^2 - \tfrac{1}{2}A(r_y-R_y)^2-\tfrac{1}{2}A(r_z-R_z)^2], \quad (10)$$

where the x direction is toward the vacancy from the site j and therefore differs for each site. It is convenient to obtain this form (10) from Eq. (9) by folding (9) with another Gaussian provided B is not allowed to be greater than A and provided A is the same in both (9) and (10). Thus since A and K and the normal lattice spacing are taken from Nosanow, we have just a four-parameter variational problem to minimize the energy $E_L=\Delta_2+E_u$. To determine the energy Δ_2 we have evaluated the two terms in Eq. (7) by the Nosanow cluster expansion. The only modification of Nosanow's expressions needed is the incorporation of the fact that not all ϕ's are the same. This difference is contained in Nosanow's expressions implicitly because each ϕ is on a different lattice site so that only a simple transliteration of his expressions is needed. In fact we still find that if only elongated Gaussians are taken for ϕ, E_{02T} of Nosanow is exactly zero. Thus to second order in the cluster expansion one obtains

$$E_L=E_{L1}+E_{L2}\ , \quad (11)$$

$$\text{where}\quad E_{L1}=\textstyle\sum_j \hbar^2(2A+B_j)/4m\ , \quad (12)$$

remembering that $B_j=A$ if j is not a first or second neighbor of the vacancy, and

$$E_{L2}=\sum_{k<l}\frac{1}{d_{kl}}\int[\phi_k{}^1(\vec{r}_k)\phi_l{}^1(\vec{r}_l)]^2$$

$$\times f^2(r_{kl})V(r_{kl})d\vec{r}_k d\vec{r}_l\,, \qquad (13)$$

where

$$d_{kl}=\int[\phi_k{}^1(\vec{r}_k)\phi_l{}^1(\vec{r}_l)]^2 f^2(r_{kl})d\vec{r}_k d\vec{r}_l\,, \qquad (14)$$

and where

$$V(r)=v(r)-(\hbar^2/2m)\nabla^2 \ln f(r)\,.$$

Here

$$v(r)=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6],$$

with $\sigma=2.556$ Å and $\epsilon=10.22°K$.

Thus except for the denominators d_{kl} in Eq. (13), if only second-cluster terms are included this problem is exactly as if the wave function were a simple product of single-particle wave functions interacting via the pseudopotential $V(r)f^2(r)$. The d_{kl} are in fact near to unity.

The undistorted vacancy energy may also be expressed by Eqs. (11)–(13), but the ϕ's must of course be spherical Gaussians undisplaced from the lattice sites. These equations when evaluated with undistorted ϕ's define E_u, E_{u1}, and E_{u2}, respectively. Then $\Delta_2=(E_{L1}-E_{u1})+(E_{L2}-E_{u2})$ and in each of these parenthesized terms use can be made of cancellations. Thus

$$(E_{L1}-E_{u1})=\sum_j{}' \hbar^2(B_j-A)/4m\,,$$

where the sum over j runs only over first and second neighbors of the vacant site. To evaluate the difference $E_{L2}-E_{u2}$ a computer program was constructed to calculate the sum in Eq. (13) for all k which are nearest and second neighbors and for all l ranging over about 1500 neighbors. This program could be run for either distorted or undistorted ϕ's, and the difference between the two results gave $E_{L2}-E_{u2}$. Although for a given set of parameters B_j, d_j there were a large number of terms to be evaluated in this program, it is not very time consuming because, with spherical Gaussians for ϕ, the numerator (or denominator) in (13) can easily be tabulated as a function of the distance between the two lattice sites. This is because only a single numerical integration is needed for each distance. Then values for the numerator or denominator of (13) could be obtained quickly by interpolation. For terms with nonspherical Gaussians the numerator or denominator of (13) evaluated for spherical Gaussians was folded with a Gaussian distribution for the location of the site in question. By interchanging the integral in (13) or (14) with the folding integral it is easily seen that the effect of the elongated Gaussian can be obtained.

To calculate the energy E_u of the undistorted vacancy relative to the ground-state energy one must (a) add one particle to the ground-state system thus increasing the energy by $\mu=PV_0+E_0$, where PV_0 is the energy associated with the expansion of one atomic volume against the external pressure, and where E_0 is the ground-state energy per particle. Then (b) subtract one particle from the lattice inside of the solid.

To discuss the ground state of the solid, we could refer to Nosanow directly but instead we note that Eqs. (11)–(13) give the ground-state energy provided the sums are interpreted as running over all lattice sites and provided the ϕ's are all spherical Gaussians centered on the lattice sites. (Thus $B_j=A$ in all cases). For convenience we will write $d_{kl}{}^{-1}$ times the integral in Eq. (13) as F_{kl}. Thus referring to Eqs. (11)–(13) interpreted as ground-state equations it can be seen that removal of a particle from site i reduces the energy by

$$\epsilon_0=3\hbar^2A/4m+\sum_l{}' F_{il}\,,$$

where the prime indicates the term $l=i$ is omitted. Furthermore the energy per particle E_0 is

$$E_0=3\hbar^2A/4m+\tfrac{1}{2}\sum_l{}' F_{il}\,,$$

where the $\frac{1}{2}$ appears because the interparticle "potential" F_{il} must not be counted twice when summing over all atoms. Thus the undistorted vacancy energy is

$$E_u=\mu-\epsilon_0=PV_0-E_0+3\hbar^2A/4m \qquad (15)$$

relative to the ground state. The last form of the expression is easily evaluated from Nosanow's results.

After the minimization of E_L is carried out, d for the first neighbors is negative (i.e., the center is moved in toward the vacancy), B is somewhat smaller than A for first neighbors indicating an elongation toward the vacancy, d for second neighbors is positive (indicating movement away from the vacancy), and $B=A$ for second neighbors (B was not allowed to be greater than A). The values of B for first neighbors and d for first and second neighbors which minimize the lower edge of the band of energies of the nonlocalized vacancy are shown in Table I. The values of E_L which correspond to these parameters are also shown in Table I. The values of E_L obtained by minimizing E_L alone are not significantly different from those shown.

IV. EVALUATION OF THE BANDWIDTH

To evaluate Eq. (5) some further generalization of the Nosanow cluster expansion must be made. Again we may transliterate Nosanow to obtain the cluster expansion for

$$E_B=H_1/N_1=\langle 1|H|2\rangle/\langle 1|2\rangle\,. \qquad (16)$$

The wave functions $|1\rangle$ and $|2\rangle$ differ only in the lo-

TABLE I. The energies Pv_0, Eu, E_L and the minimum vacancy energy E together with the parameters of the localized vacancy determined so as to minimize E, for various values of specific volume v of solid He^3. A and B are the Gaussian parameters described in the text. d_1 and d_2 are the displacements of the first- and second-neighbor atoms toward the vacant site.

v(cm^3/mole)	R(Å)	A(Å^{-2})	B(Å^{-2})	d_1(Å)	d_2(Å)	PV_0(°K)	E_u(°K)	E_L(°K)	E(min) (°K)
24.5	3.75	1.30	0.95	0.259	-0.108	10.6	21.4	14.6	9.2
22.5	3.65	1.42	0.98	0.295	-0.126	14.6	26.0	18.2	12.3
20.7	3.55	1.54	1.07	0.286	-0.122	20.1	31.3	22.1	15.9
19.0	3.45	1.65	1.14	0.278	-0.100	27.0	37.4	26.2	19.9

cation and elongation of the ϕ's. The effects of $|1\rangle$ differing from $|2\rangle$ are easily inserted in Nosanow's expansion because ϕ_i and ϕ_i^* could be treated there as two different functions. Thus we find that

$$E_B = E_{B1} + E_{B2}\,, \tag{17}$$

where

$$E_{B1} = \sum_l \int \phi_l^1(\vec{r}_l)(-\hbar^2/2m) \times \nabla_l^2 \phi_l^2(\vec{r}_l) d\vec{r}_l \equiv \sum_l C(l) \tag{18}$$

and $$E_{B2} = E_{B2V} + E_{B2T}\,, \tag{19}$$

where,

$$E_{B2V} = \sum_{k<l} \frac{1}{D_{kl}} \int \phi_k^1(\vec{r}_k)\phi_l^1(\vec{r}_l)\phi_k^2(\vec{r}_k) \times \phi_k^2(\vec{r}_l) f^2(r_{kl}) V(r_{kl}) d\vec{r}_k d\vec{r}_l\,, \tag{20}$$

$$D_{kl} = \int \phi_k^1(\vec{r}_k)\phi_l^1(\vec{r}_l)\phi_k^2(\vec{r}_k) \times \phi_l^2(\vec{r}_l) f^2(r_{kl}) d\vec{r}_k d\vec{r}_l\,, \tag{21}$$

and

$$E_{B2T} = \sum_{k\neq l} \left(\frac{1}{D_{kl}} \int \phi_k^1(\vec{r}_k)\phi_l^1(\vec{r}_l)\phi_k^2(\vec{r}_k) \times \phi_l^2(\vec{r}_l) f^2(r_{kl}) T(\vec{r}_k) d\vec{r}_k d\vec{r}_l - C(k) \right). \tag{22}$$

Here

$$T(\vec{r}_k) = (\hbar^2/2m)\{ \tfrac{1}{2}\phi_k^1(\vec{r}_k)\nabla_k^2\phi_k^2(\vec{r}_k) + \tfrac{1}{2}\phi_k^2(\vec{r}_k)\nabla_k^2\phi_k^1(\vec{r}_k) - \tfrac{1}{4}\nabla^2[\phi_k^1(\vec{r}_k)\phi^2{}_k(\vec{r}_k)]\} / [\phi^1{}_k(\vec{r}_k)\phi^2{}_k(\vec{r}_k)]. \tag{23}$$

Although shown here in detail the quantity E_{B2T} is extremely small due to cancellation in Eq. (22). There is zero contribution to Eq. (22) if ϕ_k^1 and ϕ_k^2 are both spherical Gaussians or both distorted Gaussians with the same B values along the same axis. Thus when $k=1$ (using numbering system II) the contribution to (22) is zero.

In the evaluation of these equations we have frequently made use of the fact that $\phi_k^1(\vec{r}_k)\,\phi_k^2(\vec{r}_k)$ being the product of Gaussians is itself a Gaussian. Thus, for example, calculation of E_{B2V} is entirely analogous to the calculation of E_{L2} where each atom distribution $\phi^*\phi$ is determined as the overlap $\phi_k^1(\vec{r}_k)\,\phi^2{}_k(\vec{r}_k)$. This pseudo-localized vacancy has 21 atoms which are distorted from the ground-state position or shape in a region where 22 atoms normally reside. Twenty atoms are near the original sites and one is exactly halfway between the nearest neighbor sites at which the vacancy was located before and after the jump. (In fact such an asymmetric localized vacancy, if calculated variationally, gives an energy slightly lower than the symmetric localized vacancy of Sec. II. Thus no "saddle point" in the usual sense exists for the jumping of a vacancy in bcc He^3.)

The ratio of the normalizations N_1/N_0 in Eq. (6) can be factored into a cluster product so that

$$\frac{N_1}{N_0} = \frac{\langle 1|2\rangle}{\langle 1|1\rangle} = \prod_{i=1}^{N} R_i\,, \tag{24}$$

where we have assumed

$$R_1 = \Pi_k \eta_k, \tag{25}$$

$$\eta_k = \frac{\int \phi_k^1(\vec{r}_k)\phi_k^2(\vec{r}_k)dr_k}{\int [\phi_k^1(\vec{r}_k)]^2 d\vec{r}_k}, \quad (26)$$

$$R_2 = \prod_{k<l} \frac{D_{kl}}{d_{kl}\eta_k\eta_l} . \quad (27)$$

R_i is the ratio of the factors of $\langle 1|2\rangle$ and $\langle 1|1\rangle$ obtained by factorizing these expressions according to the treatment of the quantity $M(\gamma)$ in Nosanow. It is thus possible to define all of the R so that Eq. (24) is an identity. All of the higher terms in the product are assumed to approach unity and we approximate N_1/N_0 by $R_1 \cdot R_2$. Then R_1 is easily evaluated since it only contains integrals over Gaussians and has usually been found to be about 0.05. R_2 should be close to unity since only the difference in the configuration of the pseudolocalized vacancy and the localized vacancy acting via the correlation functions f is effective. Evaluation of Eq. (27) gave about 0.9 for R_2 for all cases calculated.

We now have expressions for all of the quantities needed to evaluate Eq. (6) for Δ_1. In practice, cancellations to take place between H_1/N_1 and H_0/N_0 were taken into account in the evaluation of E_{B1} and E_{B2V} so that sums needed to be taken only over those terms in Eqs. (18) and (20) which differed from the same terms in Eqs. (12) and (13). Finally, collecting all of the above expressions we may use Eq. (8) to obtain the vacancy energy as a function of the eigenvalue X of the matrix (0, 1) and the variational parameters.

The results of the entire calculation are shown in Table I, along with the parameters of the wave function used in the calculation. The energy E in Table I corresponds to the eigenvalue $X = 8$ and is the lower edge of the vacancy band. In Table I d_1 and d_2 indicate the displacement of the first and second neighbors of the vacancy toward the vacant site. B is the Gaussian parameter in the direction of elongation for the first-neighbor atoms. The second-neighbor functions were found to be spherical when E_L was minimized and were assumed to be spherical for the calculation of E. The parameters were determined to minimize E when $X = 8$. No attempt was made to minimize E separately for various values of X, since the optimum value of the variational parameters seemed rather insensitive to the value of X. The parameters d_1, d_2, and B show some scatter since we searched on a fairly wide mesh in these variables. The mesh was small enough to determine the minimum energy value with some accuracy.

V. CONCLUSIONS

We show in Fig. 2 the energy of the localized vacancy and the lower edge of the band of energies of the nonlocalized vacancy as a function of density of solid He^3. On the same graph we have plotted the activation energies determined by various experimenters. Although the results are suggestive we have not made a detailed analysis of the specific heat or thermal conductivity or diffusion rate to be expected from such a band of vacancies, partly because the measured experimental parameters are so clearly below the calculated energies so that no close agreement could be expected. If such a comparison were made, we expect from the distribution of eigenvalues X that the energy to be compared with the experimental numbers lies about halfway between the two theoretical curves in Fig. 2.

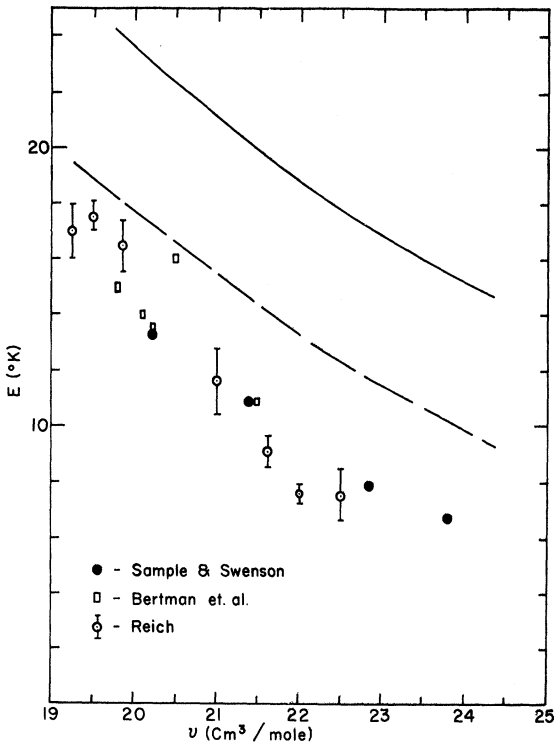

FIG. 2. The energy E of the localized vacancy (solid line) and the lower edge of the band of vacancy energies (broken line) plotted against molar volume v of solid He^3. The experimental points are those of Sample and Swenson, Bertman *et al.*, and Reich. They should be compared with an energy about midway between the two theoretical curves.

Although the energy is not in good quantitative agreement with experiment, the slope of the curve is correct. When it is recalled that the large contribution to the effect of density on the energy is through the PV_0 energy of expansion of the crystal, it seems unlikely that the interstitial energy which involves a $-PV_0$ term could give the same energy dependence. Thus the vacancy picture seems to be even more plausible in the light of the present calculation.

It would seem worthwhile, now that a specific model of the defect in He^3 exists, to calculate the vacancy energy by Monte Carlo methods in order to use the Hansen-Levesque wave function as a starting point. It could then be determined if the lowering in ground-state energy which that wave function affords will also be reflected in a lowering of the vacancy energy relative to the ground state.

There is the question of why this vacancy is only observed in the bcc structured solid He^3. We have not carried out the same calculation for the hcp lattice due to limitations in our computer program, however, we have calculated the three-dimensional wave function for a single He^3 atom in the divacancy formed by removing two He^3 atoms from a bcc lattice and compared this with the wave function for a He^4 atom in a similar divacancy in the hcp lattice. The magnitude of the wave function at the "neck" between two sites should indicate qualitatively how much neighboring atoms can move toward the vacancy and how easily the jump can be made. Because of the structure of the hcp lattice this neck is much narrower, and consequently the wave function in the neck was found to be much smaller in the case of He^4 in the hcp lattice. We expect, therefore, that when the vacancy energy calculation is done for hcp He^4 (or hcp He^3) that the energy should be much higher than for the bcc structure.

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