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# On the Magnetic Properties of Liquid He<sub>3</sub>\*.†

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The object of this paper is to investigate the possibility that liquid He<sub>3</sub> might have a tendency toward nuclear ferromagnetism in the approximation where this fluid is considered to be an antisymmetrical collection of atoms having an angular momentum of  $\hbar/2$  and a finite nuclear magnetic moment. In the rather crude approximation where the motion of the individual atoms is described with the help of plane de Broglie waves, the exchange energy, originating in the interatomic mutual potential energy of He<sub>3</sub> atoms, favors the parallel alignment of all spins at the temperature of absolute zero. The total energy of the fluid is, however, smaller in the antiferromagnetic configuration because its kinetic energy is smaller than in the ferromagnetic configuration. To the approximation of these studies then, liquid He<sub>3</sub> does not show nuclear ferromagnetism. Its nuclear paramagnetism is then discussed.

## 1. INTRODUCTION

ONE of the interesting problems raised by a collection of particles having an angular momentum of  $\hbar/2$  and a finite magnetic moment concerns its magnetic behavior. Antisymmetrical statistics resulting from first principles lead for such a collection of completely free particles to the well-known balancing of their spins and magnetic moments. At the temperature of absolute zero in such a system the total angular momentum and magnetic moment vanish. This, however, is not necessarily true if the particles of the collection exert forces upon each other. Indeed, as first shown by Bloch,<sup>1</sup> for a so-called free electron gas, in which the potential energy of any electron is constant or vanishes on the average, the Coulomb repulsion between the electrons leads to a quantum mechanical exchange energy for electrons of parallel spin. This exchange energy is negative and favors ferromagnetism. However, this energy is to be regarded as a correction to the first approximation energy (e.g., the kinetic energy) of the electrons, which is positive. Actually the preceding method of obtaining the total energy of the free electron gas may be said to be equivalent to an approximation method which proceeds according to the increasing powers of the coupling parameter,  $e^2/\hbar v_f$ , where  $v_f$  is the electron velocity at the top of the Fermi distribution associated with the antiferromagnetic configuration.<sup>2</sup> Ferromagnetism cannot occur in this model unless the coupling parameter is larger than unity. This latter condition is however equivalent to that of the breakdown in the validity of the approximation method. Within the region of validity of this method then, the free electron gas cannot exhibit ferromagnetism.

A collection of He<sub>3</sub> atoms at liquid He<sub>3</sub> densities may be regarded as approximating what one might call an antisymmetric assembly of loosely bound particles. It

appears that a study of the magnetic properties of liquid He<sub>3</sub> using the admittedly crude model of describing, in a first approximation, the motion of individual atoms by plane de Broglie waves and computing the total energy of such a system by including the mutual potential energy of He atoms, is of interest. It is realized that there will be objections to this limiting gas model. It may, however, be expected that as long as the quantum mechanical exchange energy corrections are of reasonable magnitude in comparison with the average classical potential energy or the average kinetic energy, such an approximation method would be justified.

## 2. THE TOTAL ENERGY OF LIQUID He<sub>3</sub>

In the present studies it was assumed that liquid He<sub>3</sub> stays liquid down to the absolute zero temperature, a situation often conjectured in connection with liquid He<sub>4</sub>. Since the latter fluid does not solidify down to the lowest temperature at which it has been observed, unless subjected to external pressure, it is to be expected that this conjecture is better justified in the case of liquid He<sub>3</sub> which is considerably more volatile and less dense<sup>3</sup> than liquid He<sub>4</sub>. The present investigation refers essentially to the temperature of absolute zero, where the density of the liquid was taken to be somewhat larger than the highest density observed at Los Alamos, namely  $\rho(0^\circ\text{K})$  was assumed to be 0.08 g/cc. This density determines the maximum kinetic energy or linear momentum at the top of the Fermi distributions in both the ferromagnetic ( $f$ ) and antiferromagnetic ( $a$ ) configurations. One has,  $\rho_0$  denoting the liquid density at the temperature of absolute zero, for the maximum momentum  $p_f$  and kinetic energy  $E_f$ ,

$$p_f = \hbar(3\rho_0/4\pi M)^{1/3}, \\ E_f = p_f^2/2M = (\hbar^2/2M)(3\rho_0/4\pi M)^{2/3}, \quad (1)$$

$M$  being the mass of a He<sub>3</sub> atom ( $5 \times 10^{-24}$  g), and

$$p_a = p_f/2^{1/2}, \quad E_a = E_f/2^{1/2}. \quad (2)$$

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<sup>1</sup> F. Bloch, *Zeits. f. Physik* **57**, 545 (1929).

<sup>2</sup> L. Goldstein, *J. de phys. et rad.* **7**, 141 (1936).

<sup>3</sup> See Sydorik, Grilly, and Hammel, *Phys. Rev.* **75**, 303 (1949) and Grilly, Hammel, and Sydorik, *ibid.* **75**, 1103 (1949).

The ratios of  $2^{\frac{1}{2}}$  and  $2^{\frac{1}{2}}$  between the moments  $p_f/p_a$  and kinetic energies  $E_f/E_a$  in the (*f*) and (*a*) configurations result from the inflated momentum or energy spheres in the former as compared with the latter. Indeed in the (*a*) configuration two atoms of opposite spin are accommodated per free particle state, while in the (*f*) configuration there being only one atom per state, the volume of the momentum sphere has increased by a factor two with respect to that in the (*a*) configuration.

The average kinetic energy per atom is then

$$\bar{E}_{f,a} = \frac{3}{5} E_{f,a}, \quad (3)$$

as in a completely degenerate collection of antisymmetric particles, since in our approximation the kinetic energy of an atom in liquid He<sub>3</sub> is that of a free particle within an ideal Fermi-Dirac fluid.

The total wave function of the system in the ferromagnetic configuration, normalized to unity in the volume *V*, is, in the present approximation, the determinant:

$$\psi_f(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = (N!V^N)^{-\frac{1}{2}} \sum_{P=1}^{N!} (-)^P P \times \exp[i(\mathbf{k}_1 \mathbf{r}_1 + \dots + \mathbf{k}_N \mathbf{r}_N)], \quad (4)$$

where the summation extends over all the *N*! permutations of the permutation operator *P* acting on the radius vectors  $\mathbf{r}_j$  of the He<sub>3</sub> atoms of wave vector  $\mathbf{k}_j (= \mathbf{p}_j/\hbar)$  in the system formed by *N* atoms. In the antiferromagnetic configuration the wave function is a product of two determinants associated with the (*N*/2) atoms in the two spin states respectively. Let the  $\mathbf{r}$ 's denote the radius vectors of the atoms in one spin state and the  $\mathbf{R}$ 's those of the second group of (*N*/2) atoms in the other spin state, the approximate wave function is

$$\psi_a(\mathbf{r}_1, \dots, \mathbf{r}_{N/2}, \mathbf{R}_1, \dots, \mathbf{R}_{N/2}) = [(N/2)!V^{N/2}]^{-1} \times \sum_{p=1}^{(N/2)!} \sum_{P=1}^{(N/2)!} (-)^{p+P} pP \exp\{i[(\mathbf{k}_1 \mathbf{r}_1 + \dots + \mathbf{k}_{N/2} \mathbf{r}_{N/2}) + (\mathbf{K}_1 \mathbf{R}_1 + \dots + \mathbf{K}_{N/2} \mathbf{R}_{N/2})]\}. \quad (5)$$

Here, the permutation operators *p* and *P* operate on the  $\mathbf{r}$ 's and  $\mathbf{R}$ 's respectively, the  $\mathbf{K}$ 's being the wave vectors associated with the atoms  $\mathbf{R}$  in one of the spin states. It is, of course, fully realized that the extreme ideal gas wave functions may be worse approximations here than in the case of the electron gas in the theory of metals. While in the latter case a relatively good justification can be given in some types of metals for describing the less tightly bound electrons as forming an antisymmetric assembly of practically free particles, no such justification is attempted in the present problem of liquid He<sub>3</sub>. We should like to invoke here the experimental results of the Argonne workers<sup>4</sup> on the flow properties of liquid He<sub>3</sub>. According to these results

<sup>4</sup> Osborne, Weinstock, and Abraham, Phys. Rev. **75**, 988 (1949).

the viscosity coefficient of this liquid is of the same order of magnitude as that of liquid He<sub>4</sub>I, i.e., some  $10^{-5}$  c.g.s. unit.<sup>5</sup> This in turn is of the same order of magnitude as, or somewhat larger than, the viscosity coefficient of He<sub>4</sub> vapor at liquid He temperatures. This argument should merely be considered as an indirect indication of the gas-like behavior of liquid He<sub>3</sub> where the atoms have a small but finite binding energy.<sup>6</sup>

One finds with the wave functions (5) or (6), the following potential energy of two He<sub>3</sub> atoms:

$$E_p = \frac{1}{V^2} \int \Phi(r) dv_1 dv_2 - \frac{1}{V^2} \delta(\mathbf{s}_1 - \mathbf{s}_2) \int \Phi(r) \times \exp[i(\mathbf{k}_1 - \mathbf{k}_2) \mathbf{r}] dv_1 dv_2 = E_{p,c} + E_x(|\mathbf{k}_1 - \mathbf{k}_2|). \quad (6)$$

Here,  $E_{p,c}$  is simply the classical potential energy of two stationary He<sub>3</sub> atoms averaged over their positions in the volume *V* of the fluid, with  $\Phi(r)$  denoting the mutual potential energy of two stationary atoms at a distance *r*. This was taken to be given by either one of the following two expressions due respectively to Slater and Kirkwood<sup>7</sup> and Margenau:<sup>8</sup>

$$\Phi_{S-K}(r) = A e^{-\alpha r} - B r^{-6}, \quad (7)$$

$$\Phi_M(r) = A e^{-\alpha r} - B_1 r^{-6} - B_2 r^{-8}. \quad (8)$$

In these formulas, the distance  $r = |\mathbf{r}_1 - \mathbf{r}_2|$  of the two atoms is expressed in angstrom units, the constants having the following numerical values:

<i>A</i>	<i>B</i>	<i>B</i> <sub>1</sub>	<i>B</i> <sub>2</sub>
77	0.149	0.139	$0.37 \times 10^{-11}$ erg,

while  $\alpha$  is equal to  $4.60\text{\AA}^{-1}$ .

$E_x$  is the quantum mechanical exchange energy of two He<sub>3</sub> atoms whose distance in wave vector space is  $|\mathbf{k}_1 - \mathbf{k}_2|$  while the  $\delta$ -function simply indicates that in the (*a*) configuration only atoms of parallel spin direction give rise to exchange energy ( $\mathbf{s}_1 = \mathbf{s}_2$ ). The coordinate integrations in (7) extend over the volume *V*. With the origin of the coordinate system placed at one of the atoms, one obtains

$$E_{p,c} = \frac{4\pi}{V} \int \Phi(r) r^2 dr,$$

$$E_x(k) = -\frac{4\pi}{V} \int \Phi(r) \frac{\sin kr}{kr} r^2 dr; \quad k = |\mathbf{k}_1 - \mathbf{k}_2|. \quad (10)$$

The integrals (9) and (10) diverge on account of the peculiar behavior of the interatomic potential energies (8), so that the integrations have to be cut off at some

<sup>5</sup> See the monograph of W. H. Keesom, *Helium* (Elsevier Publishing Company, Inc., Amsterdam, 1942).

<sup>6</sup> It is to be noted that the equality in order of magnitude of the liquid and vapor viscosity coefficients also holds for hydrogen but the difference in viscosities becomes increasingly large with heavy elements.

<sup>7</sup> J. C. Slater and J. G. Kirkwood, Phys. Rev. **37**, 682 (1931).

<sup>8</sup> H. Margenau, Phys. Rev. **56**, 1000 (1939).

finite small distance  $a$ . Physically, only those lower limits are acceptable which lead to a large enough negative average potential energy, since the atoms are evidently bound in the liquid. One obtains thus, at once,

$$E_{p,c}(a)_{S-K} = \frac{4\pi}{V} \left[ \frac{A}{\alpha^3} e^{-a\alpha} (2 + 2a\alpha + a^2\alpha^2) - \frac{B}{3a^3} \right], \quad (11)$$

$$E_{p,c}(a)_M = \frac{4\pi}{V} \left[ \frac{A}{\alpha^3} e^{-a\alpha} (2 + 2a\alpha + a^2\alpha^2) - \frac{B_1}{3a^3} - \frac{B_2}{5a^5} \right]. \quad (12)$$

It is found that the preceding averages become negative at values of  $a$ , such that  $a \geq 2.14A$  in the  $S-K$  case and  $a \geq 2.02A$  in the  $M$  case.

The exchange energy of a pair of  $\text{He}_3$  atoms becomes, after an elementary calculation, with the  $S-K$  potential energy,

$$E_x(k)_R = -\frac{4\pi}{V} \frac{1}{k^3} A \frac{e^{-a\alpha}}{1+\beta^2} \left[ \left( a\alpha + \frac{\beta^2-1}{\beta^2+1} \right) \sin ka + \left( ka + \frac{2\beta}{1+\beta^2} \right) \cos ka \right], \quad (13)$$

due to the repulsive part ( $R$ ) of the potential energy or the term  $Ae^{-a\alpha}$ . The attractive part, ( $A$ ), leads to:

$$E_x(k)_A = \frac{\pi B k^3}{V} \left[ \left( \frac{1}{(ka)^2} - \frac{1}{6} \right) \frac{\sin ka}{(ka)^2} + \left( \frac{1}{(ka)^2} - \frac{1}{2} \right) \frac{\cos 2ka}{3ka} + \pi/12 - \frac{1}{6} Si(ka) \right], \quad (14)$$

where

$$\beta = \alpha/k; \quad Si(x) = \int_0^x \frac{\sin x}{x} dx.$$

With the Margenau potential energy, the repulsive exchange energy is of course, the same as with the Slater-Kirkwood potential energy, while the attractive exchange term has a form similar to (14). The oscillating character of these exchange energies is of course already evident in the original formula (10).

The total energy of the liquid, in the ferromagnetic configuration becomes:

$$E_{T,f} = \frac{3}{5} N E_f + \frac{1}{2} N(N-1) E_{p,c}(a) + \frac{1}{2} \sum \mathbf{k}_1 \sum \mathbf{k}_2 E_x(|\mathbf{k}_1 - \mathbf{k}_2|). \quad (15)$$

The first term on the right-hand side is the free particle kinetic energy in a system of  $N$  atoms, with  $E_f$  being given by Eq. (1); the second term is the total classical potential energy of the system, there being  $N(N-1)/2$  pairs of energy  $E_{p,c}(a)$  per pair of atoms. Finally the last term represents the total exchange energy. In the latter, one has to sum over all possible  $\mathbf{k}$ -values of both atoms up to  $\mathbf{k}_f$ .

Similarly, in the antiferromagnetic configuration one obtains

$$E_{T,a} = \frac{3}{5} N E_a + \frac{1}{2} N(N-1) E_{p,c}(a) + 2 \left( \frac{1}{2} \sum \mathbf{k}_1 \sum \mathbf{k}_2 E_x(|\mathbf{k}_1 - \mathbf{k}_2|) \right). \quad (16)$$

In this expression, the maximum kinetic energy  $E_a$  is given by Eq. (2); the classical potential energy term is the same as in the ( $f$ ) configuration, since this quantity does not depend on the spin configuration. In the last exchange energy term, the summations over the  $\mathbf{k}$ 's extend only up to  $\mathbf{k}_a (= 2^{-1} \mathbf{k}_f)$ , the radius of the contracted wave vector sphere associated with  $(N/2)$  parallel spins, in either direction. The total exchange energy is of course the sum of the exchange energies in either spin direction, and this is indicated by the factor 2 in front of the single spin direction exchange term. We now turn to the evaluation of these exchange energies.

### 3. THE FREE PARTICLE EXCHANGE ENERGY IN LIQUID $\text{He}_3$

The summations appearing in the total exchange energy expressions in Eqs. (15) and (16) may be replaced by integrations over the distribution of free particle levels, with a level density,

$$\frac{dn(k, \theta)}{2\pi \sin \theta d\theta} = \frac{V}{(2\pi)^3} k^2 dk,$$

associated with the solid angle  $2\pi \sin \theta d\theta$  and wave vector band  $(k, k+dk)$ , so that:

$$\frac{1}{2} \sum \mathbf{k}_1 \sum \mathbf{k}_2 E_x(|\mathbf{k}_1 - \mathbf{k}_2|) = N \frac{V}{2\pi^2} \int_0^{\mathbf{k}} E_x(k) k^2 dk,$$

where the origin of the coordinate system in  $\mathbf{k}$ -space was chosen to coincide with one of the particles, say atom 1, so that an integration over the  $\mathbf{k}$ -space of this atom leads just to  $N$ , while the polar axis coinciding with the direction of  $(\mathbf{k}_1 - \mathbf{k}_2)$ , the integrand in the second integral becomes independent of the polar angle  $\theta$ , leading to a factor  $4\pi$  of the total solid angle. It is now seen that by substituting  $E_x(k)$ , as given by Eqs. (13) and (14), one obtains a series of definite integrals all expressible in terms of impractical infinite series at worst. Instead of following this procedure it appeared more useful to express the total exchange energy in another form. With the definition (10) one finds

$$\frac{1}{2} \sum \mathbf{k}_1 \sum \mathbf{k}_2 E_x(|\mathbf{k}_1 - \mathbf{k}_2|) = - \sum \mathbf{k}_2 \frac{1}{(2\pi)^2} \int \Phi(r) r^2 dr \int \frac{\sin |\mathbf{k}_1 - \mathbf{k}_2| r}{|\mathbf{k}_1 - \mathbf{k}_2| r} d\mathbf{k}_1,$$

with  $d\mathbf{k}_1$  denoting the volume element in  $\mathbf{k}_1$ -space. Choosing a polar coordinate system whose axis coincides with  $\mathbf{k}_2$ , applying the Gegenbauer addition the-

orem<sup>9</sup> to  $\sin|\mathbf{k}_1 - \mathbf{k}_2|r/|\mathbf{k}_1 - \mathbf{k}_2|r$ , integrating over  $\mathbf{k}_1$ , replacing the summation over  $\mathbf{k}_2$  by an integral with the level density  $(V(2\pi)^3)d\mathbf{k}_2$ , and integrating again one obtains finally

$$E_{x,f} = -\frac{3}{2}N \int_a^\infty \Phi(r) J_{\frac{3}{2}}^2(k_f r) \frac{dr}{r}, \quad (17)$$

where  $J_{\frac{3}{2}}(z)$  is the Bessel function of order  $\frac{3}{2}$ ,  $k_f$  and  $k_a$  denote the maximum wave vectors in the two configurations, respectively, e.g.,

$$k_f = p_f/\hbar, \quad k_a = 2^{-1}k_f.$$

Replacing, in Eq. (17),  $\Phi(r)$  by the Coulomb energy  $e^2/r$  acting between two electrons, one obtains at once the total exchange energies in the two configurations of the free electron gas model.<sup>10</sup>

In the present case of the He-He interaction the total exchange energy has no simple analytical expression. It is, however, easy to see that the exchange energy, for a chosen cut-off length  $a$ , is in general larger, the smaller the radius of the momentum or wave vector sphere of the system, a result similar to the simpler case of electrostatic coupling, where this is always true. The complication which exists in the case of helium results from a superposition of effects due to the attractive and repulsive components of the potential energy  $\Phi(r)$ .

Since a simple analytical expression of the exchange energy is lacking here, a discussion of the limitations in the validity of these calculations is not as straightforward as in the electron gas problem. A further complication arises here from the somewhat arbitrary choice of the cut-off length  $a$ . It appears, however, that the limitations on the validity of the exchange energy in the He<sub>3</sub> case should be somewhat different from those of the electron problem. In the latter because the average classical potential energy vanishes or becomes constant, the exchange energy can only be compared with

the kinetic energy or first approximation energy of the electrons. In our case, where the plane de Broglie wave approximation of the one atom wave function is postulated at the start also, the exchange energy may be compared to both the average potential and kinetic energies. Since the atoms are bound in the liquid, necessarily the potential energy is larger than the kinetic energy per atom. The comparison of the approximate exchange energy to the potential energy rather than to the smaller kinetic energy would then lead in the present calculations to a wider validity range in the wave vectors or particle densities than in the electron case.

The exchange energies have been computed here by evaluating numerically the integrals in (17).<sup>\*</sup> In all the cases studied here with the smaller Slater-Kirkwood potential energy, the exchange energy turned out to be a small fraction of both the kinetic and potential energies for the same physically significant cut-off lengths, e.g.,  $a \geq 2.2\text{\AA}$ . As expected, the exchange energy is negative for the small cut-off values, since there, the repulsive portion of the potential energy is more important than the attractive part. For cut-off lengths  $a$  which are physically significant the exchange energy starts by being negative, it then increases with increasing  $a$ , at constant  $k_f$ , becomes positive and reaches a maximum corresponding to that value of  $a$ , beyond which the potential energy  $\Phi(r)$  is negative, e.g., for  $a$  equal to the root of  $\Phi(r)$ . The positive exchange energy is associated with the predominance of the attractive part of the potential energy.

At the temperature of absolute zero, with the assumed liquid He<sub>3</sub> density, the exchange energies have been investigated with both types of potential energies and the results are given in Figs. 1 and 2.<sup>\*\*</sup> It is seen that with both types of potential energies, the exchange energy alone favors the ferromagnetic configuration since one has always  $E_{x,f} < E_{x,a}$ . However, in the whole physically significant region of the cut-off lengths, as a function of which the exchange and average potential

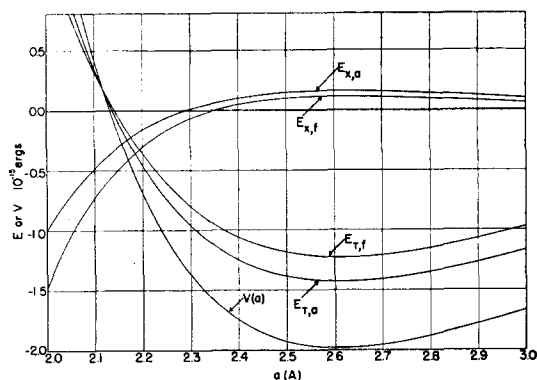


FIG. 1. Average potential, exchange, and total energies per atom in liquid He<sub>3</sub>. (Slater-Kirkwood interaction.)

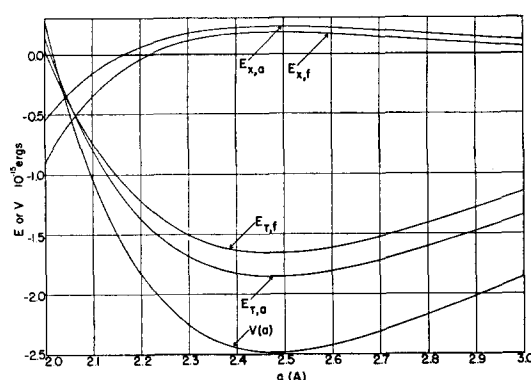


FIG. 2. Average potential, exchange and total energies per atom in liquid He<sub>3</sub>. (Margenau interaction.)

<sup>9</sup> G. N. Watson, *Theory of Bessel Functions* (Cambridge University Press, London, 1922), p. 363 or 366.

<sup>10</sup> See reference 1 or F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 341.

<sup>\*</sup> We should like to thank here Mr. D. W. Sweeney for his co-operation in this work.

<sup>\*\*</sup> One finds that the kinetic energy is  $\bar{E}_a = 4.05 \times 10^{-16}$  erg/atom.

TABLE I. Paramagnetic,  $(\chi_T/\rho)$ , and total,  $(\chi_{\text{tot}}/\rho)$ , mass susceptibilities of liquid He<sub>3</sub>.

$T$ °K	$(\chi_T/\rho)$ $10^{-7}$ c.g.s.	$-(\chi_{\text{tot}}/\rho)$ $10^{-7}$ c.g.s.
0*	0.508	5.80
0.245*	0.507	5.80
0.490*	0.504	5.81
1.2	0.478	5.83
1.5	0.464	5.85
2.0	0.431	5.88
2.5	0.404	5.91
2.8	0.391	5.92
3.1	0.384	5.93
3.34	0.400	5.91

\* These values correspond to the same liquid He<sub>3</sub> extrapolated density of 0.08 g/cc.

energies have been investigated, the total energy  $E_{T,a}$  of the antiferromagnetic configuration is smaller than that of the ferromagnetic configuration  $E_{T,f}$ . Hence, in the present, rather crude, model of liquid He<sub>3</sub> with a density value assumed at the temperature of absolute zero, the liquid would not exhibit nuclear ferromagnetism.

It is not entirely without interest to notice that with the larger Margenau potential energy there is, in a small but physically acceptable cut-off length region, some evidence for the somewhat increased stability of the ferromagnetic configuration. Clearly, it is not justifiable to attach any particular importance to this result beyond noticing its existence. The main reason for this lies in the fact that for these smaller cut-off lengths the exchange energies are about equal to the potential and kinetic energies. The validity of the exchange energy at these cut-off lengths cannot, however, be justified. This situation is similar to the one encountered in the electron case, insofar as the electron gas model leads also to ferromagnetism in the extrapolation of the approximation method to exchange energy regions where the method ceases to be valid.

We should like to add here that the model could be improved along lines suggested by Wigner's work<sup>11</sup> in the electron case. This improvement would correspond to the introduction of correlation between He<sub>3</sub> atoms of opposite spin in the antiferromagnetic configuration. It is likely that one would thus be led to a further strengthening of the conclusions reached above on the larger stability of the vanishing total spin configuration of the system.

#### 4. ON THE NUCLEAR PARAMAGNETIC SUSCEPTIBILITY OF LIQUID He<sub>3</sub>

Since our crude model of liquid He<sub>3</sub> leads to a stable non-ferromagnetic configuration, the finite nuclear magnetic moment of the He<sub>3</sub> atoms should manifest itself through a small paramagnetism of the liquid. The main interest of this paramagnetism of this liquid lies in that its experimental study might be of importance in

<sup>11</sup> E. P. Wigner, Phys. Rev. 46, 1002 (1934) and Trans. Faraday Soc. 34, 678 (1938).

showing, together with other thermodynamic properties, the possible intervention of antisymmetric statistics in the behavior of this fluid.

In the limit of the ideal antisymmetric fluid model, the paramagnetic susceptibility is given by<sup>12</sup>

$$\chi_T = \frac{n\mu^2 [-F'(\alpha)]}{kt F(\alpha)}, \quad (18)$$

where  $n$  is the atomic concentration, the spin per atom being  $\hbar/2$ ,  $\mu$  is the nuclear magnetic moment of He<sub>3</sub> ( $\mu = -1.07 \times 10^{-23}$  c.g.s.),<sup>13</sup>  $F(\alpha)$  is the statistical function determined by the temperature and concentration of the fluid according to

$$F(\alpha) = \frac{nh^3 \Gamma(\frac{3}{2})}{(2s+1)(2\pi mkT)^{\frac{3}{2}}} \\ = \frac{2}{3}(T_0/T)^{\frac{3}{2}}; \quad F'(\alpha) = dF/d\alpha,$$

with  $m$  denoting the mass of a He<sub>3</sub> atom ( $5.008 \times 10^{-24}$  g), and  $T_0$  the degeneration temperature at the concentration  $n$ ,

$$T_0 = (\hbar^2/2mk)(3n/4\pi(2s+1))^{\frac{2}{3}}.$$

At the limit of very low temperatures, e.g.,  $T \ll T_0$ ,

$$\lim_{T \ll T_0} \chi_T = \frac{3n\mu^2}{2kT_0},$$

$\chi_T$  reduces to the temperature independent Pauli paramagnetic susceptibility. The resultant magnetic susceptibility of liquid He<sub>3</sub> is the sum of its diamagnetic and paramagnetic susceptibilities. The latter is given by the Langevin formula

$$\chi_D = -n(r_0/6) \sum_{i=1}^Z \bar{r}_i^2. \quad (19)$$

Here,  $r_0$  denotes the classical electron radius ( $e^2/mc^2$ ), and  $\bar{r}_i^2$  is the mean square of the distance of the  $i$ 'th atomic electron to the nucleus, the sum being extended over all the  $Z$  electrons of the atom. The resultant or total susceptibility, per unit mass, is then

$$\chi_{\text{tot}} = (\chi_T - \chi_D)/\rho \\ = \frac{\chi_{A,D}(\text{He}_4)}{3} + \frac{\mu^2}{m_{\text{He}_3}(kT)} \frac{[-F'(\alpha)]}{F(\alpha)}, \quad (20)$$

since the atom-gram diamagnetic susceptibility of He<sub>3</sub> should be practically the same as that of He<sub>4</sub>.

Using the approximate Los Alamos liquid He<sub>3</sub> densities together with the experimental value of  $\chi_{A,D}(\text{He}_4)$  ( $= -1.90 \times 10^{-6}$  c.g.s.),<sup>14</sup> we have collected in Table I,

<sup>12</sup> L. Brillouin, *Les Statistiques Quantiques* (Les Presses Universitaires, Paris, 1930).

<sup>13</sup> H. A. Anderson and A. Novick, Phys. Rev. 73, 919 (1948).

<sup>14</sup> A. P. Wills and L. G. Hector, Phys. Rev. 23, 209 (1924); 2A, 418 (1924); G. G. Havens, Phys. Rev. 43, 992 (1933).

a series of liquid  $\text{He}_3$  susceptibilities per unit mass.<sup>15</sup> Since the diamagnetic mass susceptibility of  $\text{He}_3$  is ( $-6.31 \times 10^{-7}$  c.g.s.), it is seen that its paramagnetic mass susceptibility is but a small fraction, 6–8 percent of the former. The paramagnetic mass susceptibility is practically temperature independent in this ideal antisymmetric fluid model, in contrast with the Curie paramagnetism.

It is, of course, realized that the experimental investigation of the very feeble magnetic properties of liquid  $\text{He}_3$  would encounter serious difficulties. One of these is the problem of the establishment of statistical equilibrium in an external magnetic field necessary for the nuclear paramagnetic susceptibility to manifest itself in a physically acceptable way. It appears that an extension of the experimental methods of Bloch, Bloem-

bergen, Purcell, and Pound<sup>16</sup> to the investigation of liquid  $\text{He}_3$  could yield important information on the statistical behavior of a rather elementary monatomic system in the liquid phase. It is, indeed, clear that the understanding of the laws governing the elementary processes of energy exchange between the nuclear spin system, and the "rest" of this liquid could be of great help in furthering the knowledge of similar phenomena in more complicated systems. We should like then to conclude by saying that the experimental investigation of the magnetic properties of liquid  $\text{He}_3$  could yield, together with its other thermal properties, information regarding the possible intervention of antisymmetrical statistics in the general behavior of this fluid. Simultaneously, the nuclear paramagnetism of this liquid offers interesting possibilities in the study of approach to statistical equilibrium, in an external magnetic field and, at very low temperatures, of a unique monatomic system.

<sup>15</sup> The ratios ( $-F'(\alpha)/F(\alpha)$ ) have been obtained with the help of the tables of J. McDougall and E. C. Stoner, *Phil. Trans. Roy. Soc. London A237*, 67 (1938).

<sup>16</sup> F. Bloch, *Phys. Rev.* **70**, 460 (1946); Bloembergen, Purcell, and Pound, *Phys. Rev.* **73**, 679 (1948).

## Vibration Spectra and Normal Coordinate Treatment of Perfluorocyclobutane\*†

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The Raman spectra of gaseous and liquid cyclic  $\text{C}_4\text{F}_8$  at room temperature have been obtained and polarization measurements made for the liquid state. The infra-red absorption spectrum of the gas between 2 and  $23.1\mu$  obtained by Dr. D. C. Smith of the Naval Research Laboratory is also reported here. A normal coordinate treatment, based on the assumption that the molecular symmetry is  $D_{4h}$ , has been made and applied to assign the 23 fundamental vibration frequencies and to evaluate a set of force constants. The observed spectra have been interpreted in detail.

### INTRODUCTION

ALTHOUGH considerable interest has recently been shown in the spectroscopic properties of fluorocarbons, few papers<sup>1,2</sup> have discussed potential functions for fluorinated compounds other than methane derivatives. Values reported for C—F bond stretching force constants have ranged from 9.15 to  $3.80 \times 10^5$  dynes/cm. Perfluorocyclobutane is an example of a relatively complicated molecule which, because of its high symmetry, is amenable to a vibrational analysis. If a fairly simple potential function is assumed, force constants can be calculated for this molecule. The Raman spectrum of liquid perfluorocyclobutane has been studied by Edgell,<sup>3</sup> who also reported four infra-red

absorption maxima and made an assignment of fundamentals.

As a part of a larger project on the spectroscopic properties of fluorocarbons and fluorinated hydrocarbons the vibration spectra of perfluorocyclobutane have been investigated. This paper reports the spectra, their interpretation and a normal coordinate analysis.

### EXPERIMENTAL

The sample of perfluorocyclobutane was prepared and purified in the Jackson Laboratory of E. I. du Pont de Nemours and Company. No information was available about its purity. Since it has been possible to interpret satisfactorily all but a very few of the faintest infra-red and Raman bands, the purity is probably high.

The infra-red absorption from 2 to  $23.1\mu$  was studied by Dr. D. C. Smith of the Naval Research Laboratory by means of a prism spectrometer of high resolution.<sup>4</sup>

<sup>4</sup> Nielsen, Crawford, and Smith, *J. Opt. Soc. Am.* **37**, 296 (1947).

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<sup>1</sup> E. L. Pace, *J. Chem. Phys.* **16**, 74 (1948).

<sup>2</sup> W. F. Edgell and W. E. Byrd, *J. Chem. Phys.* **17**, 740 (1949).

<sup>3</sup> W. F. Edgell, *J. Am. Chem. Soc.* **69**, 660 (1947).