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## *Abstracts*
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# Symposium on Liquid Helium

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Prof. *Kodi Husimi* presiding

## Molecular Theory of Liquid Helium

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## The Cohesive Energy of Liquid Helium II

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It is well known that helium remains liquid at absolute zero for pressures below *25 atmos.* Its cohesive energy at zero pressure is found to be $9.7\times10^{-16}$ *erg/molecule* (*14 gram-cal/mole*) with the molar volume of *27.6 cc.*

We have calculated the cohesive energy of helium at absolute zero and zero pressure by applying the cell method. The similar calculation has already been performed by C. L. Pekeris (Phys. Rev. **79**, 1950). He has solved the Schrödinger equation for the atom in its cell and determined the energy against the volume of the liquid for the cases in which the coordination number ($z$) is equal to *12, 10* and *6* respectively. And he has concluded that the liquid helium at absolute zero has the internal structure in which the coordination number is equal to about *9.5.* According to his results, however, the minimum of the curve of energy for f. c. c. ($z=12$) is deeper than that for the case of $z=10$. So he has obtained the shallower curve in the latter case than would be expected. It seems to us that this is because he used the form of expressions which are valid only for f. c. c. in the calculations in the other case.

In our calculations we have used the same mutual potential between a pair of helium atoms as used by Pekeris, namely the one proposed by Prof. J. de Boer:

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

where $\epsilon=1.41\times10^{-15}$ *ergs*, $\sigma=2.56\times10^{-8}$ *cm* (determined from the second virial coefficient), or,

$$\varphi(r)=\epsilon[(r^*/r)^{12}-2(r^*/r)^{6}], \tag{1}$$

where $r^*=2.87\times10^{-8}$ *cm.*

The principle of our calculation is as follows. The fundamental idea of the cell method is, as is well known, that an atom of the liquid is confined to a certain "cage", formed by its neighbors, with which it suffers many collisions before being able to escape from this cell. So, if each atom ($\boldsymbol{r}_i'$) moves about the centre ($\boldsymbol{R}_i$) of each cell, the total potential energy $V(\boldsymbol{r})$ of the liquid is

$$\begin{aligned}V(\boldsymbol{r}) &= \frac{1}{2}\sum_{ij}\varphi(\boldsymbol{r}_i'-\boldsymbol{r}_j)\\ &= \frac{1}{2}\sum_{ij}\varphi(\boldsymbol{R}_{ij}+\boldsymbol{r}_i-\boldsymbol{r}_j) \qquad (\boldsymbol{r}_i'=\boldsymbol{R}_i+\boldsymbol{r}_i\,, \quad \boldsymbol{R}_{ij}=\boldsymbol{R}_i-\boldsymbol{R}_j)\\ &= \sum_{ij}\{\varphi(\boldsymbol{R}_{ij}+\boldsymbol{r}_i)-\varphi(\boldsymbol{R}_{ij})\}+\frac{1}{2}\sum_{ij}\varphi(\boldsymbol{R}_{ij})+\frac{1}{2}\sum_{ij}\{\varphi(\boldsymbol{R}_{ij}+\boldsymbol{r}_i-\boldsymbol{r}_j)\\ &\qquad -\varphi(\boldsymbol{R}_{ij}+\boldsymbol{r}_i)\}-\frac{1}{2}\sum_{ij}\{\varphi(\boldsymbol{R}_{ij}+\boldsymbol{r}_i)-\varphi(\boldsymbol{R}_{ij})\,,\end{aligned}$$

the second term being equal to $NW(0)/2$.

We can neglect the last two summations because there remain only the terms of the fourth or higher powers of $\varkappa$ when averaged over the region around the centre of each cell. Neglecting these terms and averaging on $j$ over the spheres of the nearest, the second, the third and the fourth neighbors respectively, we obtain the cage potentials formed by the respective neighbors. And thus we can reduce the problem to the one-body problem.

So our calculation consists of the following steps.

(1) First we considered the nearest neighbors only. Here, the cage potential is the same as used by Lennard-Jones and Devonshire in the classical theory of liquid. Denoting it by $V_0$, the Schrödinger equation is

$$-\frac{\hbar^2}{2m}\Delta\psi+V_0\psi=E_0\psi\,,$$

where $E_0$ is the lowest eigenvalue to be determined. As we now consider the ground state ("1*s*" state), $\psi$ is spherically symmetrical. Then, the above equation becomes

$$\frac{d^2}{dx^2}(x\psi)+\alpha(E_0-V_0)(x\psi)=0\,, \tag{2}$$

where $\alpha=2ma^2/\hbar^2$ and $x=r/a$ ($a$ is the distance to the nearest neighbors). We adopted here the boundary conditions that $d\psi/dx=0$ at $x=0$, and $\psi=0$ at $x=1$. $E_0$ is thus calculated numerically by the trial and error method for f. c. c. and for b. c. c. and is interpolated linearly between the two for the intermediate values of $z$. (Fig. 1.)

(2) Secondly we took into account the influence of the other neighbors to the eigenvalue obtained above. The cage potentials formed by the second neighbors, the third neighbors and so on are not so large compared with $V_0$ that we can apply the perturbation method for the evaluation of their contributions to the zero-point energy. We took into consideration up to the fourth neighbors for the attractive force and to the second neighbors for the repulsive one. We computed this quantity ($[v]$) for f. c. c. and b. c. c. and interpolated the two linearly for the intermediate values of $z$.

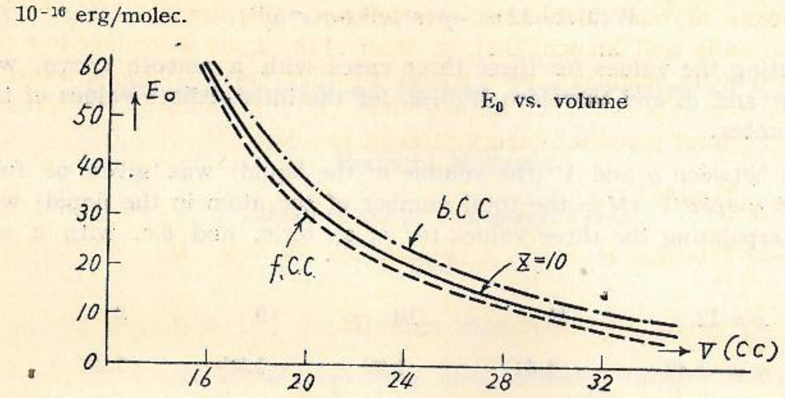

Fig. 1.

(3) Finally we must calculate the static term $W(0)/2$. This term has the form

$$\begin{aligned}W(0)/2 &= 12\epsilon[-1.20(r^*/a)^6+0.505(r^*/a)^{12}]\,, \quad \text{for f. c. c.} \quad (z=12)\\ &= 12\epsilon[-1.05(r^*/a)^6+0.381(r^*/a)^{12}]\,, \quad \text{for b. c. c.} \quad (z=8)\\ &= 12\epsilon[-0.695(r^*/a)^6+0.258(r^*/a)^{12}]\,, \quad \text{for s. c.} \quad (z=6).\end{aligned}$$

Putting, therefore, in general

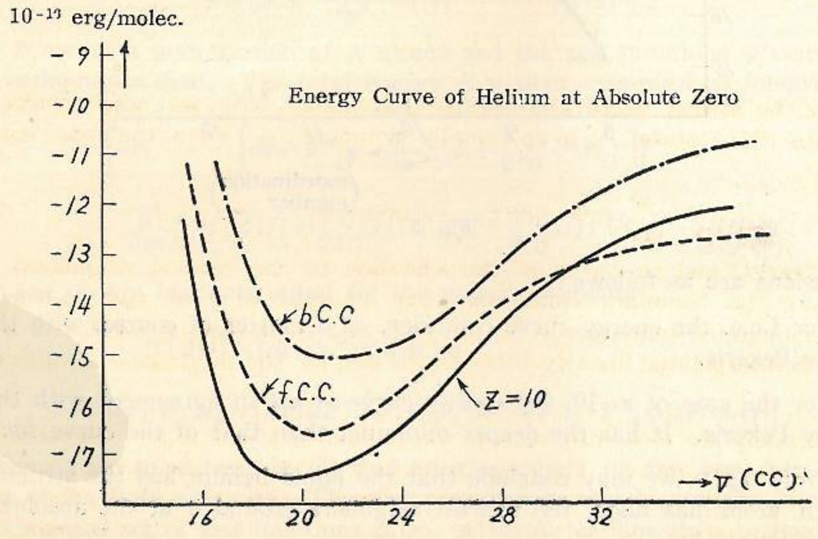

Fig. 2.

$$W(0)/2=12\epsilon\,[-p(r^*/a)^6+q(r^*/a^{12}], \tag{3}$$

and interpolating the values for these three cases with a smooth curve, we got the values $p$ and $q$, and therefore $W(0)/2$, for the intermediate values of the coordination number.

(Relation between $a$ and $V$ (the volume of the liquid) was given as follows: the value of $\gamma=Na^3/V$ ($N$ is the total number of the atom in the liquid) was obtained by interpolating the three values for f.c.c., b.c.c. and s.c. with a smooth curve; e. g.,

| | | | | |
|---|---|---|---|---|
| $z=12$ | 11 | 10 | 9 | 8 |
| $\gamma=$ 1.42 | 1.41 | 1.39 | 1.35 | 1.30 |

The energies thus calculated, i.e., $E_0+[v]+W(0)/2$, for f.c.c., b.c.c. and for the case of $z=10$ are plotted against the volume in fig. 2. The minimum of the curve for $z=10$ is deeper than the other two. If we plot the absolute values of these minima against the coordination number $z$, we obtain fig. 3. It is noticed that the maximum occurs at $z$ nearly equal to 10.

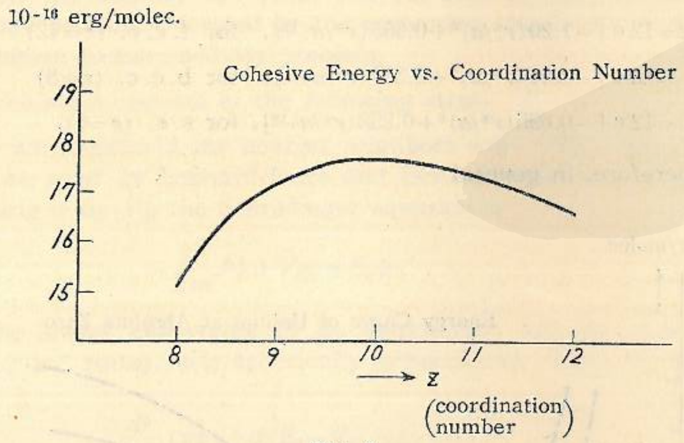

Fig. 3.

Conclusions are as follows:

(1) For f.c.c. the energy curve coincides, as a matter of course, with the one obtained by Pekeris.

(2) For the case of $z=10$, the energy curve is not in agreement with the one obtained by Pekeris. It has the deeper minimum than that of the curve for f.c.c.

(3) From fig. 3, we may conclude that the liquid helium has the structure in which each atom has about ten nearest neighbors around it at the absolute zero and zero pressure.

# Cohesive Energy of He$^4$ at Temperature O°K

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This is an attempt to calculate the cohesive energy of He$^4$ at the temperature 0°K. Such calculations have been done by several authors, but they were not always self-consistent and some were not free from unjustified assumptions.

We start from the picture of solid and adopt a body-centered cubic and a face-centered cubic lattice as the model of zero-point He, which has a structure of closest packing and has good symmetry making the calculation easy. According to this picture it seems reasonable to consider that the wave function of the total system is composed of one-body functions which are well localized about the center of the cell. In the following this will be called *cell functions.*

In correspondence to Vock's approximation in the problems of electrons, we take a permanent as the wave function of the total system:

$$\psi=(N!)^{-1/2}\sum_P \boldsymbol{P}\cdot\psi_1(\boldsymbol{r}_1)\;\cdot\;\cdot\;\cdot\;\psi_N(\boldsymbol{r}_N) \tag{1}$$

where $\boldsymbol{P}$ means a permutation of $N$ atoms and the cell functions $\psi$'s are supposed to be ortho-normalized. The total energy $E$ is then expressed as follows:

$$\begin{aligned} E&=\int d\boldsymbol{r}_1\;\cdot\;\cdot\;\cdot\int d\boldsymbol{r}_N\cdot\Psi^*\Big[-\frac{\hbar^2}{2m}\sum_i \Delta_i+\frac{1}{2}\sum_{ij}{}'V(r_{ij})\Big]\Psi \\ &=-\frac{\hbar^2}{2m}\sum_i[i\,|\,\Delta\,|\,i]+\frac{1}{2}\sum_{ij}[ij\,|\,V\,|\,ij]+\frac{1}{2}\sum_{ij}[ij\,|\,V\,|\,ji]-\sum_i[ii\,|\,V\,|\,ii] \end{aligned} \tag{2}$$

where the square brackets stand for the matrix elements

$$\begin{aligned} [i\,|\,\Delta\,|\,j]&=\int d\boldsymbol{r}\cdot\psi_i^*(\boldsymbol{r})\,\Delta_j\psi(\boldsymbol{r}) \\ [ij\,|\,V\,|\,kl]&=\int d\boldsymbol{r}\int d\boldsymbol{r}'\cdot\psi_i^*(\boldsymbol{r})\,\psi_j^*(\boldsymbol{r}')\,V(|\,\boldsymbol{r}-\boldsymbol{r}'\,|)\,\psi_k(\boldsymbol{r})\,\psi_l(\boldsymbol{r}') \end{aligned} \tag{3}$$

The sign of the third term in (2) and an appearance of the last one is characteristic of the Bose particles. The above expression can be written in terms of a non-orthogonal set of cell functions $\phi_i(\boldsymbol{r})$ in virtue of Löwdin's orthogonalization process. If we retain the terms to the first order in overlap integrals $S_{ij}$, the total energy per atom proves to be equal to

$$\frac{E}{N}=-\frac{\hbar^2}{2m}(0|\Delta|0)+\frac{1}{2}\sum_i{}'(i0\,|\,V\,|\,i0)+\frac{1}{2}\sum_i{}'(i0\,|\,V\,|\,0i)$$
$$+\frac{\hbar^2}{2m}\sum_i{}'S_{oi}(i|\Delta|0)-\sum_{ij}{}'S_{ji}[(i0|\,V|j0)+(i0|\,V\,|0j)]$$
$$+\sum_i{}'[S_{oi}(i0|\,V\,|00)+S_{io}(00|\,V|i0)] \tag{4}$$

where the parentheses ( | | ) denote the matrix elements associated with the non-orthogonal set of $\phi_i(\boldsymbol{r})$'s, $S_{oi}$ is the overlap integral $\int d\boldsymbol{r}\cdot\phi_o^*(\boldsymbol{r})\phi_i(\boldsymbol{r})$ and $\sum'_i$ means the summation over $i$ except for $i=0$.

As we are interested in the ground state, all the cell functions $\phi_i(\boldsymbol{r})$ may be assumed to have the same form about each lattice point $\boldsymbol{d}_i$:

$$\phi_i(\boldsymbol{r})=\phi(\boldsymbol{r}-\boldsymbol{d}_i), \qquad \phi_0(\boldsymbol{r})=\phi(\boldsymbol{r}). \tag{5}$$

We expand the cell function in a series of radial functions multiplied by cubic harmonics $\phi_l^{(\alpha)}(\boldsymbol{r})$ of order $l$ belonging to a specified irreducible representation $\alpha$ of the octahedral group

$$\phi(\boldsymbol{r})=r^{-1}\sum_l\phi_l(r)\phi_l^{(\alpha)}(\bar{\boldsymbol{r}}), \qquad \bar{\boldsymbol{r}}=\boldsymbol{r}/r \tag{6}$$

Cubic harmonics satisfy the orthogonality relation:

$$\int d\bar{\boldsymbol{r}}\cdot\phi_l^{(\alpha)}(\bar{\boldsymbol{r}})^*\phi_m{}^{(\beta)}(\bar{\boldsymbol{r}})=\delta_{\alpha\beta}\cdot\delta_{lm}. \tag{7}$$

As we are concerned with the zero-point oscillation, the radial function $\phi_l(r)$ will die down very rapidly with increasing $r$ and may be expanded in a series of functions of the parabolic cylinder

$$\phi_l(r)=\sum_n a_n{}^{(l)}\varphi_n(s), \qquad s=r/a, \tag{8}$$
$$\varphi_n(s)=\pi^{-1/4}2^{-(n-1)/2}(n!)^{-1/2}H_n(s)e^{-s^2/2},$$

with Hermite polynomials $H_n(s)$. The functions $\varphi_n(s)$ satisfy the orthogonality relation

$$\int_0^\infty ds\cdot\varphi_n(s)\varphi_m(s)=\delta_{nm}$$

for both even or both odd $n$ and $m$. In the expression of $\phi_l(r)$, two kinds of parameters, $a_n{}^{(l)}$ and $a$, are introduced to adjust the behaviour of probability wave and are to be determined by the variational method.

We now try to obtain the total energy in a concise form in terms of parameters $a$ and $d$ (the interatomic distance), for the case of the cell function

$$\phi_{kl\alpha}(\boldsymbol{r})=r^{-1}\phi_k(r)\phi_l{}^{(\alpha)}(\bar{\boldsymbol{r}}),$$
$$\phi_k(r)=a_k{}^{(l)}\varphi_k(s), \qquad s=r/a \tag{9}$$

The coefficient $a_k{}^{(l)}$ must be equal to $a^{-1/2}$ because of the normalization. As the Laplacian operation yields

$$\Delta[r^{-1}\phi_l(r)\phi_l{}^{(\alpha)}(\bar{\boldsymbol{r}})]=r^{-1}[\phi_l''(r)-l(l+1)r^{-2}\phi_l(r)]\phi_l{}^{(\alpha)}(\bar{\boldsymbol{r}}) \tag{10}$$

the kinetic part of the energy proves to be

$$-\frac{\hbar^2}{2m}(0|\Delta|0)=\frac{\hbar^2}{2m}\frac{1}{a^2}\left[\left(k+\frac{1}{2}\right)+l(l+1)\frac{2(k-1)!!^2}{k!}\sum_{s=1}^{\frac{k+1}{2}}\frac{(k-2s+1)!}{(k-2s+1)!!^2}\right],$$
$$\text{for odd } k. \tag{11}$$

It is seen that the kinetic energy diverges for even $k$ when the cell function $\phi_{kl\alpha}(\boldsymbol{r})$ is not spherically symmetrical, and then we must use the functions $\phi_{kl\alpha}$ with odd $k$.

The calculation of the potential part of the energy is rather troublesome. To surpass the difficulty of integration, we use Yukawa's form of mutual potential

$$V(r)=\alpha'e^{-\alpha r}/r+\beta'e^{-\beta r}/r \tag{12}$$

in place of Slater-Kirkwood's or Margenau's potential, which can be reproduced fairly well, numerically within the error of $\pm0.2\times10^{-16}$ erg in the range of $r$ from 2.5 Å to 5 Å, by choosing the values of parameters as given in Table 1.

Table 1.

| *Slater-Kirkwood's* | *Margenau's* |
|---|---|
| $\alpha=4.972$ Å$^{-1}$ | $\alpha=4.156$ Å$^{-1}$ |
| $\beta=1.208$ Å$^{-1}$ | $\beta=1.516$ Å$^{-1}$ |
| $\alpha'=+337.7\times10^{-11}$ erg. Å | $\alpha'=+36.58_4\times10^{-11}$ erg. Å |
| $\beta'=-1.842\times10^{-13}$ erg. Å | $\beta'=-6.033_7\times10^{-13}$ erg. Å |

The advantage of using Yukawa's potential lies in the fact that this type of function can be developed about two centers. The formula derived by the author is expressed as follows: If we denote the polar coordinates of two moving points $P$ and $P'$ by

$P:(r,\theta,\varphi)$ in reference to the center $O$,
$P':(r',\theta',\varphi')$ in reference to the center $O'$,

with the common polar axis $\overrightarrow{OO'}$ $(OO'=d)$, we have

$$\frac{\exp(-\alpha\cdot\overline{PP'})}{PP'}=\frac{\alpha}{2^2}\sum_{m=-\infty}^{\infty}\sum_{n=|m|}^{\infty}\sum_{n'=|m|}^{\infty}(2n+1)(2n'+1)P_n^{|m|}(\cos\theta)e^{im\varphi}P_{n'}^{|m|}(\cos\theta')e^{-im\varphi'}$$
$$\times\begin{cases}(-)^{n'}\;i_n(\alpha r)i_{n'}(\alpha r')\;K_{nn'}^{m}(\alpha d), & \text{when } r'<O'P \text{ and } r<d,\\ \phantom{(-)^{n'}}\;k_n(\alpha r)i_{n'}(\alpha r')\;I_{nn'}^{m}(\alpha d), & \text{when } r'<O'P \text{ and } r>d,\\ (-)^{n+n'}\;i_n(\alpha r)k_{n'}(\alpha r')\;I_{nn'}^{m}(\alpha d), & \text{when } r'>\overline{O'P};\end{cases} \tag{13}$$

where

$$K_{nn'}^{m}(\alpha d)=\sum_{j=m}^{\mathrm{Min}(n,n')}(-)^j\frac{(n-m)!\,(n'-m)!\,(2j-1)!!}{(n-j)!\,(n'-j)!\,(j+m)!\,(j-m)!}(\alpha d)^{-j}k_{n+n'-j}(\alpha d)$$
$$\tag{14}$$
$$I_{nn'}^{m}(\alpha d)=\sum_{j=m}^{\mathrm{Min}(n,n')}\frac{(n-m)!\,(n'-m)!\,(2j-1)!!}{(n-j)!\,(n'-j)!\,(j+m)!\,(j-m)!}(\alpha d)^{-j}i_{n+n'-j}(\alpha d)$$

and the functions $i_n(r)$ and $k_n(r)$ are the "*spherical modified Bessel functions*" of the second kind:

$$i_n(r)=\left(\frac{2\pi}{r}\right)^{1/2} I_{n+\frac{1}{2}}(r)$$

$$=\frac{1}{r}\left[e^r\sum_{j=0}^{n}\frac{(-)^j(n+j)!}{j!\,(n-j)!\,(2r)^j}+(-)^{n+1}e^{-r}\sum_{j=0}^{n}\frac{(n+j)!}{j!\,(n-j)!\,(2r)^j}\right],$$

$$k_n(r)=\left(\frac{2}{\pi r}\right)^{1/2} K_{n+\frac{1}{2}}(r)$$

$$=\frac{1}{r}e^{-r}\sum_{j=0}^{n}\frac{(n+j)!}{j!\,(n-j)!\,(2r)^j}\,. \tag{15}$$

For the sake of simplicity, we indicate the result of application of this development only for the case of the cell function having no angular part, viz. for the case of

$$\phi(\boldsymbol{r})=(4\pi)^{-1/2}r^{-1}\phi(r)\,. \tag{16}$$

$$\frac{1}{2}\sum{}'(io\,|\,V\,|\,io)$$

$$=\sum_{\alpha,\beta}\frac{\alpha'}{2}\sum_i{}'\int d\boldsymbol{r}\cdot|\,\phi(\overrightarrow{OP})|^2\int d\boldsymbol{r}'\cdot|\,\phi(\overrightarrow{O_iP'})|^2\cdot\exp(-\alpha\cdot\overline{PP'})/\overline{PP'}$$

$$=\sum_{\alpha,\beta}\frac{\alpha'\alpha}{2^3}\sum_i{}'\sum_{n=0}^{\infty}(2n+1)\Big[K^0_{nn'}\,(\alpha d_i)\int_0^{d_i}dr\phi(r)^2 i_n(\alpha r)\cdot 2^{-1}\int_{-1}^{1}d\lambda P_n(\lambda)\int_0^{\overline{O_iP}}dr'\phi(r')^2 i_0(\alpha r')$$

$$+\quad I^0_{nn'}\,(\alpha d_i)\int_{d_i}^{\infty}dr\phi(r)^2 k_n(\alpha r)\cdot 2^{-1}\int_{-1}^{1}d\lambda P_n(\lambda)\int_0^{\overline{O_iP}}dr'\phi(r')^2 i_0(\alpha r')$$

$$+(-)^n I^0_{nn'}(\alpha d_i)\int_0^{\infty}dr\phi(r)^2 i_n(\alpha r)\cdot 2^{-1}\int_{-1}^{1}d\lambda P_n(\lambda)\int_{\overline{O_iP}}^{\infty}dr'\phi(r')^2 k_0(\alpha r')\Big] \tag{17}$$

Owing to the rapidness of decay of $\phi(r)$ outside the cell, the values of two integrations are negligibly small for $d \gtrsim 3\,\text{Å}$ and hence the first only is alive, which may further be approximated fairly well by

$$\sum_{\alpha,\beta}\frac{\alpha'\alpha}{2^3}\sum_i{}' K^0_{00}(\alpha d_i)\left[\int_0^{\infty}dr\cdot\phi(r)^2 i_0(\alpha r)\right]^2 \tag{18}$$

The expressions of energy per atom for three trial functions are given below:

For $\phi_0(r)=\left(\frac{2}{\pi^{1/2}a}\right)^{1/2}\exp\left(-\frac{r^2}{2a^2}\right)$,

$$\frac{E}{N}=\frac{h^2}{8\pi^2 m}\frac{1}{2\,a^2}+\sum_{\alpha,\beta}\left[\frac{1}{2}\sum_i\frac{\alpha'\exp(-\alpha d_i)}{d_i}\right]\left[\frac{2}{\alpha a}\int_0^{\frac{\alpha a}{2}}dt\cdot e^{t^2}\right]^2. \tag{19}$$

For $\phi_1(r)=\left(\frac{2^2}{\pi^{1/2}a^3}\right)^{1/2} r\exp\left(-\frac{r^2}{2a^2}\right)$,

$$\frac{E}{N}=\frac{h^2}{8\pi^2 m}\frac{3}{2\,a^2}+\sum_{\alpha,\beta}{}'\left[\frac{1}{2}\sum_i\frac{\alpha'\exp(-\alpha d_i)}{d_i}\right]\exp\left(\frac{\alpha^2a^2}{2}\right) \tag{20}$$

For $\phi_2(r)=\left(\frac{2^3}{\pi^{1/2}3a^5}\right)^{1/2} r^2\exp\left(-\frac{r^2}{2a^2}\right)$,

$$\frac{E}{N}=\frac{h^2}{8\pi^2 m}\frac{7}{6a^2}+\sum_{\alpha,\beta}\left[\frac{1}{2}\sum_i\frac{\alpha'\exp(-\alpha d_i)}{d_i}\right]\exp\left(\frac{\alpha^2a^2}{2}\right)\left[1+\frac{\alpha^2a^2}{6}\right]^2 \tag{21}$$

It is readily seen that the potential parts in above expressions coincides with the classical one when we let $a$ tend to zero.

Through practical computations, we find that the exchange and overlap terms in the energy (4) can be neglected in our case of solid picture, since the numerical values of these prove to be of the order of $\exp\left(-\frac{d_i^2}{2a^2}\right)$ and make no essential contributions to the zero-point energy.

The numerical results will be found on the last page. (*See page 18*)

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# Atomic Theory of Liquid Helium

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In my previous paper published in 1951[1], I aimed to provide a quantum-staitstical foundation for the theory of Bose-Einstein condensation of liquid helium. But I have failed to draw out a definite conclusion about the behaviours of liquid helium near the absolute zero of temperature, because of the approximations adopted there. I should like to report on some improvement in my theory made so as to include the phonon state, which is now experimentally established at very low temperatures.

As was proved previously, the partition function $Z_N(V)$ for the system composed of $N$ identical Bose particles can be generally expressed as

$$Z_N(V)=\sum_{\{m\}}\frac{Z(m_1,\ldots\ldots,m_N)}{\prod_{l-1}^{N} m_l!\,l^{m_l}}$$

$$Z(m_1,\ldots\ldots m_N)=\sum_k\int\psi_k^*(Px)\,e^{-\beta H}\psi_k(x)\,dx\,, \tag{1}$$

where $V$ is the volume, $\beta=1/kT$, $H$ is the Hamiltonian of the system, which may be divided into two parts, the total kinetic energies $K$ and the total potential energies $\Phi$, and $P$ stands for any element of class $(m_1, m_2,\cdots m_N)$ of the symmetric group composed of $N!$ permutations operating on the $N$ coordinates $(x_1,\cdots x_N)=x\cdot m_1$ is the number of cycles of length 1 in the permutation $P$, $m_2$ that of length 2, and so on, so that $\sum_l lm_l=N$. The summation $\sum_{\{m\}}$ should be taken over all the different classes and the summation $\sum_k$ over all the wavefunctions $\psi_k(x)$ constituting a set of complete and ortho-normal (but not symmetrized) functions. For sufficiently high temperatures, $e^{-\beta H}$ may be approximated as $e^{-\beta K}e^{-\beta\Phi}$, and (1) can be approximately expressed as

$$Z_N(V)=\sum_{m_l}\prod_{l=1}^{N}\frac{(Vb_l)^{ml}}{m_l!},$$

$$b_l=\left(\frac{2\pi M_l kT}{h^2}\right)^{3/2}\frac{e^{-\beta l\Delta}}{l^{5/2}}, \tag{2}$$

where the effect of Bose statistics gives riso to an excitation of forming ring shape clusters of atoms, accompanied with an excitation energy $\Delta$ per ring bond. $M_l$'s represent the effective masses of the clusters. In deriving (2), the interactions between clusters are neglected for the sake of simplicity. For sufficiently low temperatures, the system may be, in a good approximation, described in terms of an assembly of phonons, and therefore the partition function takes the form

$$Z_{\text{phonon}}=\exp\left[\frac{4}{45}V\frac{\pi^5k^3T^3}{h^3c^3}\right], \tag{3}$$

$c$ being the velocity of the first sound. In view of an identity:

$$\sum_{\substack{\{m\}\\ \Sigma lm_l=N}}\prod_{l=1}^{N}\frac{1}{m_l!\,l^{m_l}}=1,$$

(3) can be alternatively written as

$$Z_{\text{phonon}}=\sum_{\substack{\{m\}\\ \Sigma lm_l=N}}\prod_{l=1}^{N}\frac{(a^l)^{m_l}}{m_l!\,l^{m_l}}, \tag{4}$$

where

$$a=(Z_{\text{phonon}})^{1/N}.$$

Now I shall set up an interpolating formula for the partition function, which fills the gap between (2) and (3) so as to cover whole the range of temperatures. The simplest way to this end will be to take

$$Z_N(V)=\sum_{\substack{\{m\}\\ \Sigma_l lm_l=N}}\prod_{l=1}^{N}\frac{(VB_l)^{m_l}}{m_l!} \tag{5}$$

with

$$B_l=\left(b_l+\frac{a^l}{lV}\right). \tag{6}$$

Upon assuming (5) and (6), we can discuss the condensation phenomenon rigorously, by following the same method as that used by Kahn & Uhlenbeck, who have given a rigorous theory on the condensation of classical imperfect gas[2]. A mathematical maniplulation similar to K.U.'s method yields the generating function of $Z_N(V)$ in the form

$$F(x)=\sum_{N=0}^{\infty}Z_N(V)x^N=\frac{1}{(1-at)(1-vt\chi'(t))}, \tag{7}$$

where

$$t=xe^{v\chi(t)},\qquad v=V/N$$

$$\chi(t)=\sum_{l=1}^{\infty}b_lt^l,\quad t\chi'(t)=\sum_{l=1}^{\infty}lb_lt^l. \tag{8}$$

Considering the radius of convergence $R$ of the function $F(x)$, which is related to the free energy per atom $f$ through the equation

$$R^{-1}=\lim_{N\to\infty}(Z_N)^{1/N}=\exp\left(-\frac{f}{kT}\right), \tag{9}$$

one can readily see that
for $T>T_\lambda$

$$f=kT\log t_0-vkT\chi(t_0),\quad \frac{1}{v}=t_0\chi'(t_0), \tag{10}$$

and for $T<T_\lambda$

$$f=-\frac{4}{45}v\frac{\pi^5k^4T^4}{h^3c^3}-vkT\chi\left(\frac{1}{a}\right), \tag{11}$$

and the critical temperature $T_\lambda$ is determined from

$$\frac{1}{v}=\frac{1}{a}\chi'\left(\frac{1}{a}\right). \tag{12}$$

This is the Bose-Einstein condensation. The first term in the right hand side of (11) represents the contribution from the phonons.

If one adopted, in a similar manner the expression

$$Z_N(V)=\sum_{\{m\}}\prod_{l=1}^{N}\frac{(-VB^l)^{m_l}}{m_l!}$$

for an assembly of Fermi particles, one would obtain

$$F(x)=\sum_{N=0}^{\infty}Z_N(Nv)x^N=\frac{1+at}{1-vt\chi'(t)}, \tag{13}$$

which shows no sign of phase transition as expected.

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# On the Viscosity of Liquid $He^3$

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The fundamental equation for the transport phenomena of molecular system is that called the Uhlenbeck equation. This integro-differential equation requires such tremendous efforts that we have much to do in this connection. Long ago Prof. S. Tomonaga solved it for Fermion system to estimate the viscosity and the thermal conductivity of nuclear matters. His result for viscosity can be written as

$$\eta=\frac{4}{15\sqrt{Z}\,\pi^3}\,\frac{\sqrt{m}E_0^{5/2}}{(kT)^2Q_2}\qquad(T\ll E_0/k)\tag{1}$$

in which $Q_2$ stands for a kind of cross-section which can be obtained after numerical calculation. It was found that in an example $Q_2$ is nearly equal to a one-fourth of the square of diameter, that is to say if $\sigma$ denotes the diameter of a particle then $Q_2\simeq\sigma^2/4$. Using the maximum momentum $P_0$ in place of the maximum Fermi energy $E_0$, the above equation takes the form

$$\eta\simeq\frac{16}{15}\,\frac{1}{8\pi^3}\,\frac{P_0^5}{m^2(kT)^2\sigma^2}\tag{2}$$

On the other hand, in contrary to liquid $He^4$ which obeys Bose statistics and has super-fluidity, liquid $He^3$ obeys Fermi statistics and shows a marked increase of viscosity as the temperature is lowered. This fact is undoubtedly due to the difference in statistics.

I wanted to confirm the Tomonaga's result by another method, which I have used in calculating the electric conductivity of metals at lowest temperatures. In this method the scattering processes are considered in terms of the diffusion on the Fermi-surface.

For the viscosity problem the distribution function $f$ in momentum space deviates from the Fermi function $f^0$. We write

$$f=f^0-\frac{df^0}{d\varepsilon}\chi,\qquad \varepsilon=(E-\zeta)/kT\tag{3}$$

and insert it in the Uhlenbeck equation. If degeneracy of the gas is strong $\chi$ can be regarded as a function of the point $(\Theta,\Phi)$ on the Fermi-surface. We have

$$\left(\frac{d}{dt}\chi\right)_{\text{collision}}=D\nabla^2\chi\tag{4}$$

where $\nabla^2$ denotes the Laplacian operator on the Fermi-surface and $D$ is the diffusion coefficient. We have assumed that collision of small angle predominates.

After calculation we obtain

$$D=\frac{\pi^3m^5(kT)^2}{3\,h^3P_0^2}\iint g^3w(\mathrm{g},\theta)\sin^3\theta\,d\theta\,dg\tag{5}$$

in which $g$ denotes the relative velocity of colliding particles and $w(g,\theta)$ denotes the scattering cross-section. To estimate the magnitude we make use of the hard sphere model. Then we obtain

$$D=\frac{4\pi^3}{9h^3}(kT)^2mP_0^2\sigma^2\tag{6}$$

It is convenient to express the viscosity coefficient $\eta$ as

$$\eta=G\tau\tag{7}$$

where

$$G=\frac{4}{kT}\int f^0(1-f^0)\left(\frac{m}{2}UW\right)^2d\phi=\frac{2}{3}n\langle E\rangle\tag{8}$$

($\langle E\rangle$: mean energy, $n$: number density) and $\tau$ is the relaxation time defined by

$$\left(\frac{d}{dt}\chi\right)_{\text{collision}}=-\frac{1-f^0}{\tau}\chi\tag{9}$$

For a laminar flow $\chi\sim P_2(\cos\theta)$ and we see that

$$D=P_0^2/6\tau\tag{10}$$

We are thus led to the equation

$$\eta=\frac{1}{20\pi^2}\,\frac{P_0^5}{m^2(kT)^2\sigma^2}\tag{11}$$

which is nearly identical to the Eq. (2). Thus the Tomonaga's result is comfirmed.

We may proceed to make interpolation formulas for finite temperatures. For high temperatures we have the well-known formula

$$\eta=\frac{5\sqrt{mkT}}{2^4\sqrt{\pi}\sigma^2}\tag{12}$$

If the high temperature value is adjusted

$$\eta=C\frac{\langle P^5\rangle}{m^2(kT)^2\sigma^2}\qquad\left(C=\frac{5}{2^{5/2}\cdot12\cdot2^4}\right)\tag{13}$$

gives too small value in lowest temperatures $\Big($instead of the coefficient $1/20\pi^2$ of Eq. (11) we get $\frac{5\cdot3/8}{2^{5/2}12\cdot2^4}\sim\frac{1}{700}\Big)$, and

$$\eta=C'\frac{\langle P\rangle\langle P^4\rangle}{m^2(kT)^2\sigma^2}\qquad\left(C'=\frac{1}{12\cdot2^{3/2}}\right)\tag{14}$$

gives rather large value in lowest temperatures $\Big($instead of $\frac{1}{20\pi^2}$ we get $\frac{9/28}{12\cdot2^{3/2}}\sim\frac{1}{100}\Big)$. We may assert that the correct interpolation is between these two formulas.

# Second Sound in the Mixture Liquid $He^3$—$He^4$

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It is well known that a "modified Bose-Einstein gas" model proposed originally by Bijl, de Boer, and Michels⁽¹⁾ and revised later by Toda⁽²⁾ (which is formally equivalent to Landau's roton model) represents very well most properties of pure liquid $He^4$ under its saturated vapor pressure at temperatures above *1.2°K*. In order to extend this model so as to apply to the case of $He^4$ under high pressures and to the case of $He^4$ diluted with $He^3$, the excitation energy $\Delta$ (measured by $k$) and the particle mass $M_4 (=\nu m_4,\ m_4$: atomic mass of $He^4$) are assumed to depend on the number density of $He^4$ particles, $n_4/\nu$, and the pressure $p$ (in atm) through the following relations:

$$\Delta=\Delta_0\frac{n_4/\nu}{n^0{}_4/\nu_0}\left(\frac{M_4}{M^0{}_4}\right)^{\frac{1}{3}}, \tag{1}$$

$$\nu=\nu_0+0.15(p-0.05) \tag{2}$$

where the quantities with $^0$ refer to the standard state, for which is here chosen the normal λ-point ($T=2.186°K$, $p=0.05$ *atm*).

For pure $He^4$ under pressure, eq. (1) reduces to

$$\Delta=\Delta_0\frac{\rho}{\rho_0}\left(\frac{\nu_0}{\nu}\right)^{2/3}. \tag{3}$$

Assuming ideal mixtures and neglecting the variation of $M_4$ with pressure, eq. (1) reduces to

$$\Delta=\Delta_0\frac{N_4V_4{}^0}{N_3V_3{}^0+N_4V_4{}^0} \tag{4}$$

for $He^4$ in the mixture, where $N_3$ and $N_4$ are the number of $He^3$ and $He^4$ atoms respectively and $V_3{}^0$ and $V_4{}^0$ their atomic volumes in pure liquids. $\nu_0$ and $\Delta_0$ should be determined so as to represent as well as possible the properties of pure $He^4$ under its saturated vapor pressure. The values adopted are $\nu_0=8.8$ and $\Delta_0=8.609°K$, which give the correct λ-temperature, *2.186°K*. $\nu$ and $\Delta$ for $He^4$ under pressure or in the mixture are then uniquely determined.

The calculated λ-temperature, $T_\lambda$, and the entropies on the λ-curve, $S_\lambda$, are listed and compared with experiment⁽³⁾,⁽⁴⁾ in Table I. Agreement is very satisfactory. The calculated velocity of second sound under high pressures is in moderate agreement with experiment.

The thermodynamic function of the mixture is constructed in a similar way as Heer and Daunt⁽⁵⁾ did, by assuming $He^3$ component as a nondegenerate F. D. gas and $He^4$ component as a degenerate B. E. gas, each in its own potential well. The difference of the present theory from theirs consists in using here Bijl-de Boer-Michels-Toda's B. E. gas instead of the ideal one, the excitation energy, $\Delta$, however, being considered dependent on $He^3$ concentration according to eq. (4). The λ-temperature is then given by

Table I. $T_\lambda$ and $S_\lambda - S_\lambda{}^0$ under various pressures.

| $p$ (atm) | | 0 | 5 | 10 | 15 | 20 | 25 |
|---|---|---|---|---|---|---|---|
| $T_\lambda$ (°$K$) | cal. | 2.186 | 2.125 | 2.060 | 1.991 | 1.918 | 1.850 |
| | obs. | 2.186 | 2.125 | 2.058 | 1.990 | 1.915 | 1.835 |
| $S_\lambda - S_\lambda$ (cal/g deg) | cal. | 0 | −0.0<br>23 | 43 | 61 | 76 | 90 |
| | obs. | 0 | −0.0<br>23 | 48 | 68 | 83 | 95 |

$$\frac{T_\lambda}{T_\lambda{}^0}=\left(\frac{N_4V_4{}^0}{N_3V_3{}^0+N_4V_4{}^0}\right)^{2/3}\exp\left[\frac{2}{3}\left(\frac{\Delta}{T_\lambda}-\frac{\Delta_0}{T_\lambda{}^0}\right)\right]. \tag{5}$$

The calculated λ-temperature is in good accord with experiment⁽⁶⁾,⁽⁷⁾ at lower concentrations ($\lesssim 50\%$ $He^3$), but the agreement is somewhat worse for higher concentration solutions, whose λ-temperatures lie below *1°K*. It is to be noted that the assumption of concentration-independent excitation energy leads to complete disagreement with experiment. The vapor pressure and the distribution coefficient are also calculated along the line of Heer and Daunt's theory. Agreement with experiment is good also in this case. Henry's law constant $h$ is expressed, in the present theory, as

$$h=p_3{}^0\frac{V_3{}^0}{V_4{}^0}\exp\left[1-\frac{1}{\nu}\frac{V_3{}^0}{V_4{}^0}\left(\frac{\Delta_0}{T}+1\right)x_0\right], \tag{6}$$

where $x_0$ is the normal fraction in pure $He^4$. In Fig. 1, the calculated Henry's law constant divided by $p_3{}^0$ is compared with the experimental values derived from Sommers' observed vapor pressure data. For comparison, the result of calculation according to the de Boer-Gorter-Taconis theory is also included. The experiment decisively favors the "B.E. liquid" theory.

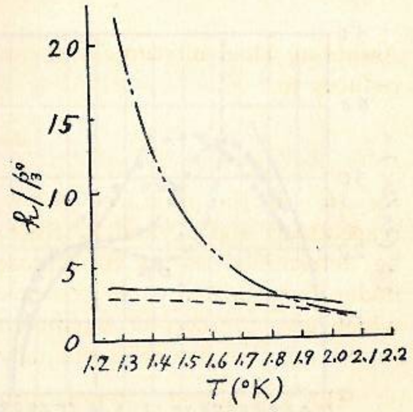

Fig. 1. Henry's law constant divided $p_3{}^0$. Solid curve: B.E. liquid theory. Dot-dashed curve; de Boer and Gorter's theory. Dashed curve: experimental curve derived from Sommers' vapor pressure data⁽⁸⁾.

The velocity of second sound in the mixture calculated on two different assumptions: in Case A, $He^3$ is assumed to move with the same velocity as the normal part of $He^4$, and in Case B, $He^3$ is assumed to be stationary with the center of gravity system. According to the "B.E. liquid" above described, the velocity in a dilute solution is given by

$$v_{II}^2=\frac{1}{1+\frac{x_3}{x}-x_3}\left[\frac{1-x}{1-x_0}v_{II}^{0\,2}+\frac{2}{3}\frac{R}{\nu}\frac{V_3^0}{V_4^0}\frac{x_3(1-x)\,(\varDelta+T)\left(\frac{\varDelta}{T}+\frac{5}{2}\right)}{\frac{\varDelta}{T}+\frac{3}{2}}\times\right.$$
$$\left.\left\{1-\frac{\varDelta}{T}\frac{1}{\left(\frac{\varDelta}{T}+\frac{3}{2}\right)\left(\frac{\varDelta}{T}+\frac{5}{2}\right)}\right\}^{-1}+\frac{RT}{3}(1-x_3)\,(1-x)\frac{x_3}{x}\right]\quad\text{for Case A,}\qquad(7)$$

and

$$v_{II}^2=\frac{1-x}{1-x_0}[v_{II}^0]^2\qquad\text{for Case B,}\qquad(8)$$

where $x_3=\rho_3/\rho_3+\rho_4$, $x=\rho_{4n}/\rho_4$. According to de Boer and Gorter's theory, it is

$$v_{II}^2=\frac{1}{1+\frac{x_3}{3}-x_3}[v_{II}^0]^2_\tau\qquad\text{for Case A,}\qquad(9)$$

and

$$v_{II}^2=[v_{II}^0]^2_\tau+\frac{RT}{3}\frac{(1-x_3)\,(1-x)}{1+\frac{4}{3}\frac{x_3}{x}-x_3}\frac{x^3}{x}\qquad\text{for Case B,}\qquad(10)$$

where $[v_{II}^0]_\tau$ means the velocity in pure He$^4$ at the temperature $\tau$, such as $[x_0]_\tau=[x]_T$. Among the above four formulas, only the two, i.e. the first and the last ones, are found to be consistent with experiment at temperatures above *1.3°K*. Below this temperature nothing can be said without introducing the influence of phonons, except at very low temperatures (see below). It is interesting that this two allowable cases correspond to different assumptions concerning the behavior of He$^3$. As de Boer and Gorter's view is inconsistent with the experimental facts on vapor pressure, it appears plausible to conclude that the above result confirms the correctness of Case A. The same conclusion can be deduced from considerations regarding the second sound in the mixture near $T=0$. The formulas (6) and (9) are probably valid also at sufficiently low temperatures, when phonons play no important role compared with that of He$^3$. As easily found from (6), the "B.E. liquid" theory then predicts that $v_{II}$ in a dilute solution decreases in $\sqrt{T}$ in this temperature region. According to de Boer and Gorter's theory, on the contrary, it must tend to the same limiting value as that in pure He$^4$, as is seen from (9). Recent experiment by King and Fairbank(9) seems to have confirmed broadly the $\sqrt{T}$-dependence of $v_{II}$ in the mixture near $T=0$. Fig. 2 shows the theoretical $v_{II}$ according to (6) compared with

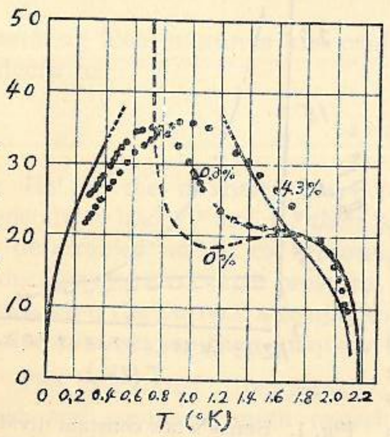

Fig. 2. Velocity of second sound in mixtures He$^3$–He$^4$. Solid curve: B. E. liquid theory. Experimental points: King and Fairbank(9).

King and Fairbank's experiment.

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## Title is not known

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## SYMPOSIUM ON LIQUID HELIUM

(***Continued from P. 9***)

### R. Nozawa and B. Sha's Paper

Of three trial functions, the first one (19) gives the lowest energy. Results of the numerical computation are shown in Table 2 and 3, where the values of $a^{-1}$ are indicated which give the lowest value of $E/N$ for the specified values of the interatomic distance.

Table 2.
For $\phi_0(r)$ and b.c.c. model.

| $d$ in Å | $a^{-1}$ in Å$^{-1}$ | $E/N$ in $10^{-16}$ *erg/atom* |
|---|---|---|
| 2.6 | 3.2 | $-16.0$ |
| 2.8 | 2.7 | $-46.0$ |
| 3.0 | 2.2 | $-44.3$ |
| 3.3 | 1.8 | $-31.9$ |
| 3.8 | 1.3 | $-13.5$ |
| 4.0 | 1.2 | $-\ 9.4$ |

Table 3.
For $\phi_0(r)$ and f.c.c. model.

| $d$ in Å | $a^{-1}$ in Å$^{-1}$ | $E/N$ in $10^{-16}$ *erg/atom* |
|---|---|---|
| 2.6 | 3.4 | $-46.8$ |
| 2.8 | 2.8 | $-83.0$ |
| 3.0 | 2.3 | $-77.1$ |
| 3.3 | 1.8 | $-54.6$ |
| 3.8 | 1.4 | $-24.2$ |
| 4.0 | 1.3 | $-17.0$ |

It may be said that the above values are reasonable if compared with the experimental data:

Liquid: $-9.7\times10^{-16}$ *erg/atom*
for $d = 3.90$ Å (b.c.c. model)
and $d = 4.02$ Å (f.c.c. model).

Solid: $-9\times10^{-16}$ *erg/atom*
for $d = 3.59$ Å (b.c.c. model)
and $d = 3.69$ Å (f.c.c. model).

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# Ferri- et Anti-ferromagnétisme

par Louis Néel

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Depuis une quinzaine d'années d'importants progrès ont été accomplis dans nos connaissances sur les propriétés magnétiques des corps, notamment en ce qui concerne le ferrimagnétisme et l'antiferromagnétisme. L'interprétation de leurs propriétés résulte d'une extension de la notion d'aimantation spontanée: dans la conception primitive de P. Weiss, il s'agit de l'aimantation de domaines suffisamment petits dans lesquels les moments magnétiques de tous les atomes possèdent la même direction. On admet actuellement la possibilité d'une subdivision du réseau primitif en sous-réseaux: dans chaque sous-réseau, les moments des atomes possèdent la même direction mais cette direction diffère d'un sous-réseau à l'autre. Deux exemples de telles subdivisions sont aujourd'hui connus avec certitude: celui de deux sous-réseaux inégaux à aimantations antiparallèles (ferrimagnétisme) et celui de deux sous-réseaux égaux à aimantations antiparallèles (antiferromagnétisme). Dans les deux cas, les interactions entre sous réseaux différents jouent un rôle prépondérant. Bien d'autres possibilités peuvent être conçues théoriquement: C. Kittel en a étudié quelques unes, mais aucune n'a encore été reconnue avec certitude du point de vue expérimental.

L'existence de ces sous-réseaux a été confirmée expérimentalement d'une manière directe par Shull et ses collaborateurs en utilisant la diffraction des neutrons, aussi bien pour le ferrimagnétisme ($Fe_3O_4$) que pour l'antiferromagnétisme (MnO par exemple). Cependant, dans certains cas comme celui du manganèse dont des arguments d'ordre magnétique font présumer la nature antiferromagnétique, cet ordre n'a pas été retrouvé, du moins avec le degré convenable, par diffraction neutronique: peut-être se produit-il au cours du temps une permutation des sens d'aimantation des deux sous-réseaux trop rapide vis-à-vis de la vitesse des neutrons pour qu'une diffraction régulière s'établisse. Une autre preuve directe mais encore plus frappante de l'existence des deux sous-réseaux a été fournie par E.W. Gorter et se rapporte à un ferrite mixte de lithium et de chrome: quand on chauffe cette substance, préalablement aimantée à basse température, son aimantation rémanente s'annule réversiblement et change de signe aux environs de 100°C pour disparaître irréversiblement comme d'habitude au point de Curie, vers 300°C. Ce phénomène prévu théoriquement provient d'une évolution thermique différente de l'aimantation spontanée des deux sous-réseaux, l'une plus grande impose son signe à basse température, tandis que c'est l'autre qui l'emporte à haute température.

Des preuves indirectes de l'existence des deux sous-réseaux résultent de la confirmation expérimentale des prévision de la théorie relatives à l'aimantation à saturation des ferrites simples de Cu, Ni, Co, Fe, Mn et des ferrites obtenus à partir des précédents par substitution partielle de zinc à l'ion divalent. Cependant des désaccords apparaissent parfois dont l'origine peut être multiple : l'incertitude sur le degré de blocage du moment orbital ; l'incertitude sur la place exacte des ions dans le réseau et sur leur degré d'ionisation, l'existence possible de surstructures secondaires à l'intérieur d'un sous-réseau ; enfin les défauts de stoechiométrie, les électrons de conduction peuvent aussi jouer un rôle.

L'interprétation de la variation thermique des propriétés magnétiques des antiferro—et ferri-magnétiques présente un gros intérêt mais soulève, si l'on désire tant soit peu de rigueur, des difficultés insurmontables : on sait en effet que pour les ferromagnétiques ordinaires nous ignorons encore la solution exacte, relative à trois dimensions, d'un problème aussi simplifié que celui d'Ising. Ici, le problème est compliqué par la grandeur des moments atomiques mis en jeu, par le nombre élevé des intégrales d'échange à considérer : 9 intégrales différentes pour le ferrite de cuivre, à ne considérer que les voisins les plus proches. On sait d'ailleurs que cela ne suffit pas : de considérations que j'ai développées autrefois à propos du nickel et qui reprennent aujourd'hui une certaine actualité, semble résulter la nécessité de prendre en considération les interactions avec une centaine de voisins au moins, sinon un millier. Le mécanisme de ces interactions éloignées pourrait d'ailleurs s'apparenter au superéchange de Kramers et Anderson. Bien des problèmes restent d'ailleurs posés à propos de ce superéchange : c'est ainsi que dans les ferrites il faudrait éclaircir les interactions importantes qui existent entre les sites tétraèdriques (sites A) et qui semblent mettre en jeu six atomes d'oxygène et appartenir au type M–O–O–M.

Il est donc indispensable de traiter ces problèmes par des méthodes approchées : en particulier l'extension aux ferrites de la méthode du champ moléculaire, avec trois coefficients indépendants caractéristiques des interactions AA, AB et BB a fourni des résultats très intéressants et permis d'interpréter beaucoup de résultats expérimentaux comme l'allure hyperbolique si remarquable de la courbe représentative de l'inverse de la susceptibilité paramagnétique en fonction de la température ou la variation thermique de l'aimantation à saturation, avec l'allure, très variées selon la substance, des courbes représentatives, les unes presque linéaires entre le zéro absolu et le point de Curie, les autres avec passage au zéro et changement de signe à une certaine température de compensation. Quelques difficultés subsistent néanmoins : l'inverse de la pente de l'asymptote à l'hyperbole de la susceptibilité devrait être égale à la constante de Curie de la somme des ions présents. Or on trouve en général des valeurs plus fortes. Ces écarts doivent être attribués, tout au moins pour une part, à la variation thermique des coefficients de champ moléculaire provenant de la dilatation et de l'agitation thermique. J'ai attiré depuis longtemps l'attention sur l'importance de cette correction de dilatation qui, toutes choses égales d'ailleurs, est proportionnelle au coefficient de champ moléculaire : elle est très importante dans les ferrites où, malgré un point de Curie parfois très bas, les coefficients de champ moléculaire sont grands. La valeur de cette correction peut se déduire des anomalies de dilatation : on peut ainsi rendre compte quantitativement de la valeur trop élevée de la constante de Curie asymptotique de la magnétite. Dans le ferrite de magnésium, la correction de dilatation ne suffit pas à rendre compte des anomalies observées : un autre phénomène doit

intervenir, probablement le déplacement progressif des ions Mg qui, sous l'influence de l'agitation thermique, tendent à se placer au hasard sur les sites A et les sites B.

Dans les antiferromagnétiques, les valeurs des températures de Curie et de disparition de l'ordre sont liées par une relation qui dépend de la valeur des intractions et de la disposition relative des sous-réseaux. Il est donc assez tentant de déduire de la valeur de ces températures des renseignements sur cette disposition. Malheureusement l'existence de la correction de dilatation enlève toute valeur à cette méthode. Par ailleurs il est certain que la température de disparition de l'ordre doit être modifiée d'une façon importante par les fluctuations du champ moléculaire.

Enfin, et surtout dans les antiferromagnétiques, les couplages de la direction d'antiferromagnétisme avec le réseau jouent un rôle important. Si ces couplages n'existent pas, la direction d'antiferromagnétisme est toujours perpendiculaire au champ appliqué, et, comme l'a montré autrefois L. Néel, la susceptiblité reste indépendante de la température aussi longtempe que l'ordre presiste. Il semble que ce soit le cas de $Fe_2O_3$ $\alpha$, dans un plan perpendiculaire à l'axe : dans ce plan en effet la susceptibilité est indépendante de la température et la direction d'antiferromagnétisme doit tourner librement dans ce plan. En général il existe des orientation privilégiées de la direction d'antiferromagnétisme, liées au réseau cristallin, pour lesquelles l'énergie est minimum. C'est tout-à-fait l'analogue des directions privilégiées de l'aimantation spontanée des ferromagnétiques, à cette différence près que l'action d'un champ extérieur appliqué doit être beaucoup moins efficace que pour les ferromagnétiques, car ce champ n'agit que sur une composante paramagnétique induite faible de l'aimantation au lieu d'agir sur l'aimantation spontanée tout entière. Citons cependant le cas du chlorure de nickel hydraté, étudié par C. J. Gorter, Poulis et autres, où on a provoqué le découplage de la direction d'antiferromagnétisme au moyen d'un champ extérieur, dans des circonstances analogues avec celles qui avaient été prévues antérieurement.

Lorsque les directions d'antiferromagnétisme sont orientées au hasard, la valeur de la susceptibilité au zéro absolu est égale au 2/3 de sa valeur à la température de disparition de l'ordre. A mon avis, il n'y a pas lieu d'attacher beaucoup d'importance à la vérification ou à la non-vérification de cette relation qui peut être plus ou moins modifiée par les fluctuations du champ moléculaire et par la correction de dilatation.

Il doit exister dans les antiferromagnétiques, comme dans les ferromagnétiques, des domaines élémentaires qui correspondent aux régions à l'intérieur desquelles la direction d'antiferromagnétisme conserve partout la même orientation, mais nous ne savons rien de plus à leur sujet car ils sons beaucoup moins accessibles à l'expérience que les domaines élémentaires des ferromagnétiques. Sous l'action d'un champ extérieur, la direction d'antiferromagnétisme tend à s'orienter dans un plan perpendiculaire à celui-ci : il en résulte une augmentation de la susceptibilité proportionnelle au carré du champ, signalée d'abord par L. Néel, puis étudiée en détail par Nagamiya et ses collaborateurs et qui paraît correspondre à des faits expérimentaux observés par Bizette et Tsaï. Il faut cependant faire remarquer qu'à côté des changements d'orientation de la direction d'antiferromagnétisme à l'intérieur des domaines élémentaires, doit se produire en même temps un déplacement des parois de séparation entre les domaines dont le premier stade est un déplacement réversible proportionnel au carré du champ auquel correspond un terme proportionnel dans l'expression de la susceptibilité. Un calcul rapide montre que ce second terme, essentiellement lié aux imperfections du réseau, peut fort bien dépasser de beaucoup le premier.

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