KCl. Commercial material had the highest slope. In zone-purified material, the slope was lower. It was also suppressed in material doped with calcium.

(3) The increase of coloring rate due to deformation that had been observed previously was confirmed. However, there were indications that as the samples were irradiated more and more heavily, the coloring curves tended to approach each other again. Deformation had no effect whatsoever on the F- to M-center relationship.

(4) It was determined that changes in the ratio of M and F centers brought about by bleaching could be reversed by short re-irradiation. Moreover, luminescence was observed in the crystals under gamma irradiation, the spectral distribution and intensity of which was observed to differ in various samples. It is thought possible that the square relation between the M- and F-center concentration is due to an equilibrium under irradiation conditions.

Hartree Calculations for the Ground State of Solid He and other Noble Gas Crystals*

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A single-particle model in which the wave functions are spherically symmetric about each lattice site was used to calculate the ground-state energy E_0 of solid He. The self-consistent Hartree equations (which yielded the best such wave functions) were solved numerically to an accuracy of better than 1%. The results were worse than could have been expected a priori: At the observed densities, the calculated values of E_0 were approximately +34 and +14 cal/mole for He³ and He⁴, respectively, as compared with experimental values of −4.5 and −12 cal/mole. Previous calculations are discussed in the light of our results. In addition, we calculated E_0 for the crystals of the other noble gas elements. The results for Ar, Kr, and Xe are within experimental error whereas E_0 for Ne is definitely outside this error (being about 5% higher than experiment).

I. INTRODUCTION

IN the last few years the properties of solid He³ have received considerable attention both theoretically and experimentally.[1] The fact that He³ has a nuclear spin of $\frac{1}{2}$ makes it possible to do a variety of experiments on it (e.g., measurements of the magnetic susceptibility, longitudinal and transverse relaxation times, and self-diffusion coefficient) which are not possible with He⁴. The crucial point in understanding these phenomena theoretically is the calculation of the effect of Fermi-Dirac statistics and exchange forces on the properties of solid He³. Such a calculation requires a detailed knowledge of the wave function of solid He³. The object of this note is to present our recent computer calculations of the ground-state energy and wave function of solid He³ and to discuss previous calculations[2–4] in the light of our results. In addition, we will also present calculations of the ground-state properties of crystals of the other noble gas elements.

The difficulty of computing the low-temperature properties of solid He² arises from the fact that its kinetic energy is of the same order of magnitude as its potential energy; this is due to the low mass of He³ and the weakness of the attraction between two He atoms. Because of the relatively large kinetic energy, an external pressure of about 30 atmospheres is necessary to solidify He³. Under these conditions He³ has a body-centered cubic structure which is to be contrasted with the close packed structures of He⁴ and the other noble gas elements.[5] In addition, the average deviation of a He³ atom from its equilibrium position is certainly of the order of 30–40% of the nearest-neighbor distance;

[1] *Helium Three,* edited by J. G. Daunt, (Ohio State University Press, Columbus, Ohio, 1960).

[2] N. Bernardes and H. Primakoff, Phys. Rev. Letters **2**, 290 (1959); **3**, 144 (1959); Phys. Rev. **119**, 968 (1960).
[3] N. Bernardes, Phys. Rev. **120**, 1927 (1960).
[4] E. M. Saunders, Phys. Rev. **126**, 1724 (1962).
[5] J. Vignos and H. Fairbank, Phys. Rev. Letters **6**, 265 (1961), have recently found a new ("high" temperature) phase of He⁴ which almost certainly has the bcc structure.

this is roughly the same as in He⁴, but about ten times as large as the average deviations in the other noble gas crystals.[2,6] Therefore, it is certainly not possible to treat solid He³ or He⁴ by the method of small oscillations which is usually used to treat crystals.

To gain some insight into this problem, we felt that it was worthwhile to use a computer to calculate the lowest energy which could be obtained from a variational treatment using a wave function written as a product of single-particle wave functions which are spherically symmetric about each lattice site. The single-particle wave functions which minimize the ground-state energy are then solutions of the well-known Hartree equations. These equations can be solved by iteration and are, therefore, well suited to computer calculations. We have calculated the ground-state energy and wave function in this way for crystals of all of the noble gas elements. The numerical results, which are valid to within 1%, are presented in Tables II and III.

Before discussing these results for He it is illuminating to consider crystals of the other noble gas elements Ne, Ar, Kr, and Xe. In these systems it is a good approximation to expand the potential energy about the lattice sites and retain only quadratic terms. This approximation allows the Hartree equations to be solved analytically yielding a simple algebraic expression containing lattice sums. The results of this solution are presented in column 3 of Table II where they are compared with the results of Bernardes.[6] They yield values of the ground state energies of crystals of Ne, Kr, and Xe which are within experimental error; the result for Ar is outside experimental error but only by about 1%. The numerical solution of the Hartree equation, given in column 4 of Table II, changes the results of this simple calculation slightly in that the result for Ar is now within experimental error and the result for Ne is definitely outside the experimental error, being about 5% too high.

The above calculations already indicate serious difficulties with He since the corrections to the Hartree approximation appear to be increasing at least as fast as the inverse square of the mass of the atom. Our results for He³ and He⁴ show that this is indeed the situation (see Table III). For a nearest-neighbor distance consistent with the observed density the calculated values of the ground-state energies are approximately +34 and +14 cal/mole for He³ and He⁴, respectively, as compared with experimental values of approximately −4.5 and −12 cal/mole. The values of the wave function and self-consistent potential for a typical calculation for He³ are given in Fig. 1.[7]

These results, whose agreement with experiment is far worse than could be anticipated *a priori*, clearly point out the inadequacy of a model for solid Helium

[6] N. Bernardes, Phys. Rev. **112**, 1534 (1958).
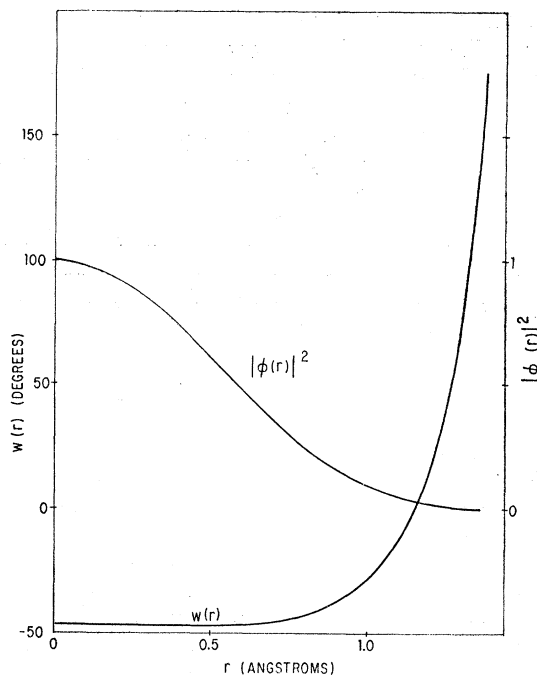[7] See discussion in Sec. III associated with Fig. 1.

FIG. 1. Plot of the self-consistent potential $w(r)$ (in units of degrees) and the square of the single-particle wave function (in arbitrary units) as a function of the magnitude r of the deviation of a particle from its lattice site for He³.

with single-particle wave functions which are spherically symmetric about each lattice site. The Hartree equations for a crystal describe the motion of the ith particle in a self-consistent potential w_i which is the sum over all neighbors j of the two-body interactions v_{ij} averaged over the motions of atoms j. Consider v_{ij} to have a hard core of radius r_c.[8] The Hartree procedure effectively extends this radius by an amount given by the deviation of an atom from its lattice site. Thus, w is a potential well with infinitely high walls in *all directions*, and there are no divergences in the energy as in a liquid or nuclear matter. On the other hand, because of this infinite repulsion, there can be no overlap or exchange interaction in a single-particle model. In addition, we have assumed that the single-particle wave functions were spherically symmetric about their lattice sites. This neglect of the "symmetry of the lattice" (i.e., the configurational symmetry of the atoms in a particular lattice structure) required additional averaging which eliminated the dependence of w_i on direction and further decreased the volume of the attractive well.

From the above discussion it is clear that a calculation of the binding energy of solid helium must include the effect of (i) the symmetry of the lattice and (ii)

[8] Actually, the form of v is not well known at very small distances. However, the repulsion is so strong that for *discussion* purposes we may consider v to have a hard core. In fact, detailed knowledge of this repulsion is very likely needed in order to accurately predict quantities such as the exchange energy.

correlations between the motions of two (or more) atoms. The latter effect might be treated by introducing a K matrix as is done in the theory of liquid He[3] or nuclear matter.[9] It is our opinion that it is necessary to include *both* of the above effects accurately to obtain a good answer. Although it seems likely that, taken independently, (ii) would give a much larger correction than (i), but the contributions from (i) and (ii) are certainly *not* independent. To see this, we note that including the correlations would increase the "size" of the well considerably, and thus emphasize the importance of specific directions in the motion of the atom. Without correlations, the effective size of the wall is too small for this to have a large effect on the energy.

We shall now discuss the relationship of our work to previous work on this subject. Bernardes and Primakoff[2] gave a variational treatment for He[3] using spherically symmetric Gaussian single-particle wave functions with an "effective" interaction, constructed by modifying the true two-body interaction at small distances and chosen to reproduce the gross experimental properties of He[4] fairly well. In this manner they included the effect of correlations in a phenomenological way[10]; this allows the wave functions to overlap. Their calculations give rather good agreement as far as gross properties of solid He[3] are concerned; however, experiments[1] show that they have overestimated the exchange effects. In fact, it is not at all clear that such a calculation can even give the correct order of magnitude of the exchange integral. Even if such a treatment gave a good representation of the correlations in He[4], the differences in mass and crystal structure between He[3] and He[4] would alter the effective interaction. The tail of the wave function, to which the exchange integral is very sensitive, depends strongly on the precise form of the repulsive part of the effective interaction. This was already apparent in the calculations of Brueckner and Gammel,[9,11] who found that the Yntema-Schneider potential (whose repulsive part rises less rapidly than that of the Lennard-Jones potential) gave a reasonable binding energy, whereas the Lennard-Jones potential gave a slightly higher answer which resulted in a wrong sign for this energy. In addition, they found[11] that it was necessary to include accurately the interaction for distances small enough so that the potential reached a value of about 10^4 deg, which further emphasizes the sensitivity of the tail of the wave function to the repulsive part of the interaction. Finally, since the exchange energy is so small, a simple analytic form of the wave function could easily give a reasonable binding energy with an exchange energy that is unreliable.

The paper by Bernardes[3] considers only the gross properties of solid He. His treatment contains the same physical assumptions as ours does, but uses an approximate numerical method which involves an expansion in powers of the kinetic energy and a variational calculation with a one-parameter sinusoidal wave function. If his treatment were carried out *exactly*, it would have to yield a higher energy than we obtained. Since Bernardes obtained energies which were lower than ours by a factor of two or three, his method converges too slowly for use with He.

Saunders[4] has included both the effects of correlation and symmetry by using a Jastrow-type wave function. Employing physical arguments, he reduced the calculation to a two-body problem, which he then solved so as to include the symmetry of the lattice. Since it is difficult to justify some of his approximations in a systematic way, and since he obtains an energy of the order of $+10$ cal/mole, it is hard to estimate the error in his calculation of the exchange energy.

Our results for Ne, Ar, Kr, and Xe give only a slight improvement over the results obtained by Bernardes.[6] However, since our results are the *best* values that can be obtained with a spherically averaged single-particle theory, it is clear that the effects of correlations and symmetry contribute about 5% of the ground state energy of neon, although they contribute much less for Ar, Kr, and Xe. Since these effects are small, but definitely present in Ne, it would very likely be feasible and certainly worthwhile to try to calculate them. If this were done, it might shed considerable light on the more difficult calculation of the properties of solid helium.

II. HARTREE TREATMENT

We consider a system of N atoms of mass m described by positions r_i relative to lattice sites R_i $(1 \leq i \leq N)$. The Hamiltonian for the system is

$$H = -(\hbar^2/2m)\sum_i \nabla_i{}^2 + \sum_{i<j} v_{ij}, \qquad (2.1)$$

where $v(|R_i + r_i - R_j - r_j|)$ is the potential of interaction between two atoms. The potential is usually written in the Lennard-Jones form,

$$v(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \qquad (2.2)$$

where ϵ and σ are usually determined from the measurements of the second virial coefficient. The values of ϵ in units of 10 deg and σ in angstroms for the noble gas elements are given in Table I. For helium the Yntema-Schneider potential,

$$v(r) = \epsilon_0[1200 \exp(-4.82r) - 1.24r^{-6} - 1.89r^{-8}], \qquad (2.3)$$

is also used; $\epsilon_0 = 7250$ deg and r in angstroms.[9]

Our program is to do a variational calculation of the ground-state energy of such a system under the condi-

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[9] K. A. Brueckner and J. L. Gammel, Phys. Rev. **109**, 1040 (1958) and previous papers referred to therein.

[10] Although symmetry effects are not included explicitly, they must enter implicitly in determining an effective v to fit the experimental results on He[4].

[11] K. A. Brueckner (private communication).

TABLE I. Values of the Lennard-Jones parameters ϵ and σ and the nearest-neighbor distance A; these are all taken from Bernardes.[a]

	ϵ (10 deg)	σ (Å)	A (Å)
He	1.02	2.56	
Ne	3.62	2.74	3.13
Ar	12.1	3.40	3.76
Kr	16.3	3.65	4.01
Xe	23.2	3.98	4.35

[a] See reference 6.

TABLE II. Values of $-E_0$ for Ne, Ar, Kr, and Xe in units of kcal/mole; minima are obtained at the observed nearest-neighbor distances given in Table I. The parentheses contain the kinetic energies for our numerical solutions.

			Hartree calculations	
	Experiment[a]	Bernardes[b]	Oscillator approximation	Numerical solution
Ne	0.450±0.010	0.420	0.457	0.431 (0.085)
Ar	1.850±0.012	1.852	1.875	1.859 (0.097)
Kr	2.59 ±0.05	2.63	2.64	2.63 (0.073)
Xe	3.83 ±0.05	3.82	3.83	3.83 (0.065)

[a] See reference 13.
[b] See reference 6.

tion that the wave functions have the form

$$\Psi=\prod_i \varphi(\mathbf{R}_i+\mathbf{r}_i),\qquad(2.4)$$

where

$$\varphi(\mathbf{R}_i+\mathbf{r}_i)=u(r_i)/(4\pi)^{\frac{1}{2}}r_i,\qquad(2.5)$$

and

$$\int_0^\infty |u(r)|^2dr=1.\qquad(2.6)$$

That is, we look for the best wave function which is a product of single-particle wave functions, each of which is spherically symmetric about a lattice site. It is straightforward to show that $u(r)$ is the lowest energy solution of the Hartree equation,

$$-(\hbar^2/2m)u''(r)+w(r)u(r)=eu(r),\qquad(2.7)$$

with the boundary conditions $u(\infty)=0$ and $\lim_{r\to0}[u(r)/r]$ =finite. The self-consistent potential $w(r)$, which depends on $u(r)$, is given by

$$w(r)=\sum_j{}'\int_0^\infty v_s(R_j,\rho,r)|u(\rho)|^2d\rho,\qquad(2.8)$$

where

$$v_s(R_j,\rho,r)=(16\pi^2)^{-1}\int d\Omega_r\int d\Omega_\rho\, v(|\mathbf{R}_j+\varrho-\mathbf{r}|).\quad(2.9)$$

In (2.7) the particle can be looked upon as localized about the lattice site at the origin so that the sum in (2.8) runs over all neighbors. The spherical averages over the angles of ϱ and $\mathbf{r}$ in (2.9) enter because of the spherical symmetry of $u(r)$. The ground-state energy per particle of the system is given by

$$E_0=e_0-\frac{1}{2}\int_0^\infty |u(r)|^2w(r)dr,\qquad(2.10)$$

where e_0 is the lowest eigenvalue of (2.7).

Before discussing the numerical solution of (2.7), it is illuminating to obtain an approximate solution analytically. We shall consider the case that the atoms perform only small oscillations about the lattice sites. Then $v(|\mathbf{R}_j+\varrho-\mathbf{r}|)$ can be expanded in powers of ϱ and $\mathbf{r}$ and integrations in (2.9) carried out explicitly. When terms in ϱ and $\mathbf{r}$ higher than quadratic are

neglected, (2.8) becomes

$$w(r)=w_0+\tfrac{1}{2}w_2(r^2+\int_0^\infty \rho^2|u(\rho)|^2d\rho),\qquad(2.11)$$

where

$$w_0=\sum_j{}' v(R_j),\qquad(2.12)$$

and

$$w_2=\tfrac{1}{3}\sum_j{}'\left(\frac{d^2v(R_j)}{dR_j{}^2}+\frac{2}{R_j}\frac{dv(R_j)}{dR_j}\right).\qquad(2.13)$$

With (2.11) it is straightforward to solve for the lowest energy state of (2.7) appropriate to the boundary conditions. The ground-state single-particle wave function and energy per particle turn out to be

$$\varphi(r)=(\alpha^{3/2}/\pi^{3/4})\exp(-\alpha^2r^2/2),\qquad(2.14)$$

and

$$E_0=\tfrac{1}{2}[w_0+3\hbar(w_2/m)^{\frac{1}{2}}],\qquad(2.15)$$

where $\alpha^2=(mw_2)^{\frac{1}{2}}/\hbar$. It is easy to evaluate (2.15), since w_0 and w_2 can be calculated in terms of known lattice sums.[12] We have done this for all of the noble gases except He; the results are given in Table II. These results compare favorably with those of Bernardes.[6] Equation (2.14) cannot apply to He, since the He atoms perform very large oscillations about each lattice site. This shows up in that w_2 calculated for the measured lattice distance in He is negative.

III. NUMERICAL SOLUTION

We obtain the single-particle potential and wave function, $w(r)$ and $u(r)$, from the Hartree equations, (2.7) and (2.8), by iteration. The main numerical difficulty is that $w(r)$ must be evaluated at many points for each iteration. As can be seen from (2.8) and (2.9), calculation of $w(r)$ for a given r requires the evaluation of a three-dimensional integral. In addition, the potential can become infinite over part of the region of integration. This causes no difficulty in principle, because the wave function which multiplies it will always vanish sufficiently strongly so that there will

[12] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954).

TABLE III. Values of $+E_0$ for He^3 and He^4 for various nearest-neighbor distances (in angstroms) in units of cal/mole. The nearest-neighbor distances for both He^3 and He^4, determined from the observed densities, are about 3.7 Å. The Lennard-Jones form of the potential was used. The parentheses contain kinetic energies.

A	Experiment[a]	Hartree calculation 3.65	3.70	3.80	4.20
He^3(bcc)	-4.5 ± 0.5		37.2	34.5 (71.8)	27.9
He^3(fcc)		36.4 (87.4)	34.6 (83.0)	31.8 (75.4)	
He^4(fcc)	-12 ± 0.3	14.4	13.9	13.1	

[a] See reference 13.

be no spurious infinities. However, a numerical cutoff procedure is clearly indicated.

To handle both of these difficulties, we note that for values of R_j, ρ and r such that $|R_j+\varrho-r|$ never vanishes, the integrals in (2.9) can be carried out explicitly for the potentials given by (2.2) and (2.3). One finds for the Lennard-Jones potential

$$v_s(R_j,\rho,r) = (\epsilon/R_j\rho r)[f_{LJ}(R_j+\rho+r)$$
$$+f_{LJ}(R_j-\rho-r)-f_{LJ}(R_j+\rho-r)$$
$$-f_{LJ}(R_j-\rho+r)], \quad (3.1)$$

where

$$f_{LJ}(r)=0.0111\sigma^{12}r^{-9}-0.8333\sigma^6r^{-3}, \quad (3.2)$$

and for the Yntema-Schneider potential

$$v_s(R_j,\rho,r) = (\epsilon_0/4R_j\rho r)[f_{YS}(R_j+\rho+r)$$
$$+f_{YS}(R_j-\rho-r)-f_{YS}(R_j+\rho-r)$$
$$-f_{YS}(R_j-\rho+r)], \quad (3.3)$$

where

$$f_{YS}(r)=10.716(2+4.82r)\exp(-4.82r)$$
$$-0.1325r^{-3}-0.0630r^{-5}. \quad (3.4)$$

Our cutoff procedure consisted in choosing a distance g and then using either (3.1) or (3.3) in (2.8) whenever $R_j-\rho-r>g$ and

$$v_s(R_j,\rho,r)=nv(g), \quad (3.5)$$

whenever $R_j+\rho-r\leq g$ (n is the number of nearest neighbors). The calculation was carried out for several g's and it was always possible to find a g_0 such that E_0 was unchanged for any $g<g_0$.

In calculating $w(r)$, it is also necessary to evaluate the sum over the lattice sites. Using tabulated values[12] of the distances of various shells from a given atom and the number of atoms in each shell, we included the first 34 shells for a fcc lattice and the first 38 shells

for a bcc lattice. In both cases this included all atoms up to 6 nearest-neighbor distances from the central atom and gave the lattice sums to an accuracy of better than half a percent.

Once $w(r)$ is tabulated, the next step is to solve the differential Eq. (2.7) numerically. We calculated E_0 for various step sizes H from 0.001 to 0.005 Å keeping all other parameters fixed. From the variation of E_0 with H we could set an accuracy on our results of better than 1% for He and better than $\frac{1}{2}$% for the other noble gas elements.

The results for Ne, Ar, Kr, and Xe are given in the last column of Table II; they are presented for the measured nearest-neighbor distances[6,13] given in Table I, since the calculated E_0 is a minimum at these distances. The results for He^4 (fcc structure) and He^3 (fcc and bcc structures) are given in Table III for various nearest neighbor distances A. There is no minimum in the variation of E_0 with A as is to be expected since crystalline He exists only under pressure.

The extremely poor agreement of the He results with experiment should be compared with the excellent agreement for the rest of the noble gas elements. The self-consistent potential for these elements, as shown in Sec. II, can be very closely approximated by an oscillator potential. On the other hand, the self-consistent potential for He, a typical example of which is shown in Fig. 1, is much more like a square well. Therefore, we have also calculated the lowest energy which could be obtained with a wave function $\varphi(r)$ of the form sinar using the same parameters as in Fig. 1. We found E_0 approximately $+42$ cal/mole, which is about 20% higher than the Hartree result. This discrepancy is due almost entirely to the fact that the Hartree $\varphi(r)$ tails off more slowly than sinar.

Calculations of the binding energy of He analogous to those in Table III were also performed using the YS potential (2.3). They gave results which in all cases were essentially the same as those obtained with the LJ potential (2.2).

ACKNOWLEDGMENT

[13] E. R. Dobbs and G. O. Jones, *Reports on Progress in Physics* (The Physical Society, London, 1957), Vol. 20, p. 516.