Experimental values of the stopping power of metal foils for lithium ions at energies considerably above the range of our experiments are available.[8,9] Wilcox measured the stopping power of gold for Li^6 ions from $_4Be^9(p,\alpha)Li^6$ at approximately 810 kev. In Table II Wilcox's value is listed as applying to Li^7, by giving the energy at which Li^7 has the same velocity as an 810-kev Li^6 ion. The data on Au, Cu, and Al are from Devons and Towle, who used Li^7 ions from $Be^9(d,\alpha)Li^7$.

TABLE II. Stopping power of metals for Li^7 ions.

Kinetic energy (Mev)	Atomic stopping power in units of 10^{-15} ev $\times$cm^2/atom Al	Cu	Au
0.944	...	...	123
2.74	112	166	208

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[8] H. A. Wilcox, Phys. Rev. 74, 1743 (1948), Fig. 4.

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Validity of the Assumption of Two-Body Interactions in Molecular Physics*

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The treatment of three-body van der Waals forces between hydrogen or helium atoms, given in an earlier paper, is extended to the heavy rare gas atoms. Two of the three atoms are supposed to be close together (e.g., nearest neighbors in a crystal), whereas the third atom is considerably farther away. Expressions are given for the induced dipole-dipole and dipole-quadrupole components of the field. The electronic charges in the atoms are represented by Gaussian distribution functions. The results are applied to a determination of the most stable crystal structure of the heavy rare gases at absolute zero temperature (excluding zero-point energy); it is found that the face-centered cubic crystal is favored over the hexagonal close-packed by about one-tenth of one percent of the van der Waals cohesive energy, if the first and second shells of neighbors are excluded from the region of summation for the third atom. If this restriction is dropped, then the difference between the two structures vanishes, while the effect itself rises abruptly and very steeply. The effect of three-body interactions in general is to weaken the attractive forces in the crystalline state. Under the above restriction, the relative magnitude of these interactions is twenty percent of the van der Waals cohesive energy for xenon. The three-body forces vanish identically if the Gaussian goes over into a Dirac δ function.

INTRODUCTION

THE evaluation of the partition function for a system of N-interacting atoms or molecules is usually carried out in two steps. First, the eigenvalues of the energy are found for a system of two fixed atoms as a function of the distance between their centers of mass. Then these eigenvalues are used as pair-potential functions in the Hamiltonian for a simplified system of N point particles. Much of the empirical research in molecular physics has been based on this procedure and has concentrated on finding more and more accurate two-body potential functions to describe properties of dense systems. There exists in the literature a variety of different potential functions with different numbers of parameters which have been obtained empirically from analyses of different physical phenomena (second and third virial coefficients, viscosity, and heat conductivity of gases, compressibility of molecular crystals; especially, argon, Debye characteristic temperatures, etc.). Moreover, an explanation of the stability of the cubic close-packed crystal structure of the heavy rare gases on the basis of any two-body potential function has been unsuccessful.[1–4] All the results of such calculations indicate the hexagonal close-packed lattice to be more stable, although it is favored over the cubic by only one hundredth of one percent of the cohesive energy. In addition to this problem, there may be other physical phenomena which cannot be explained qualitatively on the basis of two-body interactions.

Deviations from the principle of two-body forces occur when the finite extension of the atomic charges is taken into account. It is logical to consider such many-body forces as a perturbation of the Hamiltonian for point particles; then the different corrections are obtained in the corresponding orders of perturbation theory.[5] The relative importance of these different-order corrections varies with the density of the system.

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[1] T. Kihara and S. Koba, J. Phys. Soc. Japan 7, 348 (1952).

[2] T. Kihara, Revs. Modern Phys. 25, 831 (1953).

[3] Prins, Dumoré, and Tjoan, Physica 18, 307 (1952).

[4] T. H. K. Barron and C. Domb, Proc. Roy. Soc. (London) A227, 447 (1955).

[5] The point-particle basis for a perturbation treatment implies that the expansion of many-body forces in terms of simultaneous interactions among increasing numbers of atoms converges rapidly, in which case interactions among clusters of more than three atoms may be neglected.

At low densities, where a simple-product type of zero-order wave function for the system of interacting atoms may be used, the first nonvanishing correction occurs in the third order; at very high densities the first order is predominant. The third-order dipole-dipole correction has been found by Axilrod and Teller to favor the cubic crystal, but not sufficiently to insure its absolute stability.[6,7] First-order forces are of such short range that they affect mainly the twelve nearest neighbors around a central atom. Comparing the two crystals, one finds that only three of the twelve nearest neighbors have different positions. Rosen's first-order calculation[8] for three helium atoms may be shown to favor hexagonal structure by a very small amount.[9]

In a previous publication[10] (hereafter referred to as I), we have suggested that the stability of the cubic structure may arise from a three-body force in *second*-order perturbation theory. Two of the three atoms should be neighbors in the crystal and, therefore, represented by an antisymmetric zero-order wave function; otherwise there would be no triplet term in the second order. Numerical results were given for dipole-dipole interactions between three hydrogen atoms with parallel spins and three helium atoms. In this paper we will extend the calculations to include the heavy rare gases, using a Gaussian distribution function for the atomic charges. Since the results indicate that the triplet dipole forces constitute an appreciable portion of the cohesive energy of the crystals, the triplet dipole-quadrupole interactions are also evaluated. The result is summed over a finite portion of the cubic and hexagonal close-packed crystal structures.

FORMALISM

For the calculation of the second-order energy of interaction between three heavy rare gas atoms, we can use a procedure similar to that outlined in I. Consider two of the atoms A and B to be nearest neighbors while the third atom C is farther away. The second-order energy is given by

$$W''=-(H'^2)_{00}/2E_{\mathrm{Av}},\tag{1}$$

where E_{Av} is a mean excitation energy of the atom and $H'=H_{AC}'+H_{BC}'$. The justification for using this partial Hamiltonian has been given in I. Since the distance from atom C to either A or B is large compared with the nearest-neighbor distance in the crystal, a multipole expansion may be used for H_{AC}' and H_{BC}'. The zero-order wave function is

$$\Psi_0=\{\sum_\lambda(-1)^\lambda P_\lambda\varphi_A\varphi_B\}\varphi_C.\tag{2}$$

Here φ_A is an antisymmetrized wave function for atom A, etc., and P_λ is the permutation operator for exchange of pairs of electrons between A and B. Even if the wave functions for the heavy atoms were known with sufficient accuracy, the evaluation of $(H'^2)_{00}$ would be extremely complicated. However, the use of a much simpler representation of the charge distribution in the atom may be justified. In I it was shown that the second-order energy for hydrogen or helium atoms is of the form

$$W''=W_0''/(1-\Delta^2)+W''_{\mathrm{exch}},\tag{3}$$

where Δ is the overlap integral for atoms A and B and W_0'' is the second-order energy summed pairwise. Since the contribution of three-body interactions is calculated as a relatively small difference between two large quantities (W'' and W_0''), it seems as if using only approximate wave functions might invalidate any conclusion about the sign and magnitude of the three-body effect. This is not true, however, because W'' equals W_0'' plus a correction so that the use of approximate wave functions affects only the three-body term itself. The contribution W''_{exch} involves exchange of electrons between A and B. For hydrogen atoms only a single interatomic exchange is possible, in helium a double exchange also occurs, and in heavier atoms multiple exchanges are possible. An additional complication in the case of the heavy atoms is that the interatomic and intraatomic exchanges may be coupled. For example, if i_A, j_A, k_B, l_B represent four orbitals on atoms A and B, and 1, 2, 3, 4 are four electrons, then the matrix element for the single-exchange integral is given by

$$\langle i_A(1)k_B(3)|H'^2|i_A(3)k_B(1)\rangle.$$

The coupled exchanges may have the following forms:

$$\langle i_A(1)j_A(2)k_B(3)|H'^2|i_A(3)j_A(1)k_B(2)\rangle$$

and

$$\langle i_A(1)j_A(2)k_B(3)l_B(4)|H'^2|i_A(4)j_A(1)k_B(2)l_B(3)\rangle,$$

etc. We have determined the relative magnitude of such coupled exchange terms by calculating them for neon atoms using the wave functions of Brown[11] as modified by Bleick and Mayer.[12] We found that coupled exchange is an order of magnitude less important than single exchange contributions. Furthermore, the results for helium obtained in I indicate that a double exchange process gives a negligibly small contribution compared with single exchange except at very small interatomic distances. We have verified that this is also true for neon; for helium and neon the ratio of double to single exchange is of the order of Δ^2.

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[6] B. M. Axilrod and E. Teller, J. Chem. Phys. **11**, 299 (1943).

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[8] P. Rosen, J. Chem. Phys. **21**, 1007 (1953).

[9] Three-body forces in the first order of perturbation theory can be evaluated equivalently by the method of molecular orbitals; this was done for alkali metals by Löwdin [P. O. Löwdin, J. Chem. Phys. **19**, 1570, 1579 (1951)] and for a linear array of three helium atoms by A. Shostak [J. Chem. Phys. **23**, 1808 (1955)].

[10] R. McGinnies and L. Jansen, Phys. Rev. **101**, 1301 (1956).

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By extrapolation of the results for helium and neon to the heavier rare gases, it seems reasonable to assume that also for heavier atoms only single interatomic exchange needs to be considered. This makes it possible to use a collective model for the negative charge distribution of the atom, and we choose for convenience a Gaussian distribution function with adjustable width.[‡] The three-body interactions for heavy atoms become then formally the same as the expressions for three hydrogen atoms, the dipole-dipole part of which was given in I. [See I, Eqs. (11) and (12).] An antisymmetric character is inserted in the Gaussian-type wave function by this analogy with the hydrogen-like wave functions. The various exchange integrals must be evaluated using a Gaussian distribution function:

$$\rho(r_A)=(\beta/\pi^{\frac{1}{2}})^3\exp(-\beta^2 r_A{}^2), \tag{4}$$

where r_A is the distance from the nucleus at A. There are similar expressions for $\rho(r_B)$ and $\rho(r_C)$.

EVALUATION OF THREE-BODY FORCES

(a) Dipole-Dipole Interaction

The perturbation Hamiltonian H_{AC}' for dipole-dipole interactions is given by

$$H_{AC}'=\mathbf{p}_A\cdot\mathbf{T}_{AC}\cdot\mathbf{p}_C, \tag{5}$$

where $\mathbf{p}_A$ is the dipole vector $\sum_i e_i\mathbf{r}_i$ of atom A, $\mathbf{p}_C$ that of atom C, and $\mathbf{T}_{AC}$ is a second-rank tensor defined by

$$\mathbf{T}_{AC}=\frac{1}{R_{AC}{}^3}\left[\mathbf{U}-3\frac{\mathbf{R}_{AC}\mathbf{R}_{AC}}{R_{AC}{}^2}\right]. \tag{6}$$

The distance between the centers of mass is R_{AC}, and $\mathbf{U}$ is the unit tensor. The second-order energy W'' is evaluated using the same coordinate systems as in I, Fig. 2. The result can be taken directly from that for three hydrogen atoms; the integrals Δ, I_2 and I_3 [defined in Eq. (10) of I] have the following forms:

$$\Delta=\exp(-\mu^2),\quad I_2=I_3=\Delta/2\beta^2, \tag{7}$$

where $\mu=\beta R_{AB}/2$.

We are interested in the relative deviation from the principle of two-body forces; i.e., in the ratio $(W''-W_0'')/W_0''{}_{(ABC)}$, with

$$W_0''{}_{(ABC)}=W_0''{}_{(AB)}+W_0''{}_{(BC)}+W_0''{}_{(AC)},$$

the pairwise second-order dipole interaction between A, B, and C. As in I, the result depends on the particular triangular configuration. A convenient way to express it is in terms of the interior angles γ_1, γ_2, and γ_3 of the triangle A, B, C. The following final result is then obtained:

$$\left[\frac{W''-W_0''}{W_0''{}_{(ABC)}}\right]_{d-d}=\frac{4\mu^2\Delta^2}{3(1-\Delta^2)}\times\left[\frac{1}{R_{AC}{}^6}+\frac{1}{R_{BC}{}^6}-\frac{3}{4}\left(\frac{\sin^2\gamma_1}{R_{AC}{}^6}+\frac{\sin^2\gamma_2}{R_{BC}{}^6}\right)+\frac{1}{2R_{AC}{}^3R_{BC}{}^3}(2-3\cos^2\gamma_3+3\cos\gamma_1\cos\gamma_2\cos\gamma_3)\right]\times\left[\frac{1}{R_{AB}{}^6}+\frac{1}{R_{AC}{}^6}+\frac{1}{R_{BC}{}^6}\right]^{-1}. \tag{8}$$

TABLE I. Characteristic parameters for heavy rare gases.

Element	$\epsilon\times10^{16}$ (ergs)	σ(A)	E_{Av} (ev)	R(A)	β(A^{-1})	μ	$\Delta^2/(1-\Delta^2)$
Neon	49.14	2.749	21.56	3.20	1.07	1.72	2.71×10^{-3}
Argon	165.3	3.405	15.76	3.84	0.623	1.20	0.0609
Krypton	229.3	3.652	14.00	3.94	0.532	1.05	0.125
Xenon	317.2	3.937	12.13	4.37	0.454	0.993	0.162
(Helium)	(14.11)	(2.55)	(24.5)	(3.60)	(1.59)	(2.87)	

The parameter β in the Gaussian distribution function may be determined by calculating the second-order dipole interaction between two atoms and equating the result to the London expression or, equivalently, to an empirical expression such as the Lennard-Jones potential. The second-order dipole energy between two atoms a distance R apart in terms of β is

$$W_0''=-\frac{3e^4}{4\beta^4R^6E_{\text{Av}}}=-\frac{4\epsilon\sigma^6}{R^6}, \tag{9}$$

where ϵ and σ are the Lennard-Jones parameters. Then

$$\beta^4=\frac{3e^4}{16\epsilon\sigma^6E_{\text{Av}}}. \tag{10}$$

Table I gives the values for $\mu=\beta R/2$ for the rare gases, using the nearest-neighbor distance in the crystals for R.

The values for β increase slowly from xenon to argon, but the value for neon is much larger than that for the heavier atoms. This indicates that a Gaussian distribution function is not a good approximation for the charge distribution in neon atoms.

(b) Dipole-Quadrupole Interactions

The Hamiltonian H_{AC}' for dipole-quadrupole interactions between atoms A and C has the form

$$H_{AC}'=\tfrac{1}{2}\mathbf{p}_A\cdot\nabla\mathbf{T}_{AC}:\mathbf{q}_C-\tfrac{1}{2}\mathbf{p}_C\cdot\nabla\mathbf{T}_{AC}:\mathbf{q}_A. \tag{11}$$

Here, $\mathbf{T}$ is the tensor already defined and $\mathbf{q}=\sum_i e_i\mathbf{r}_i\mathbf{r}_i$ is the quadrupole tensor of an atom. The matrix ele-

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[‡] The fact that only single interatomic exchange has to be taken into account and that coupled exchanges may be neglected implies that the effect depends sensitively only on the general shape of the charge distribution of the atom and not on the precise form of the wave function. R. H. Tredgold and R. U. Ayres (private communication) have fitted the outer region of a Hartree-Fock wave function for argon with a Gaussian function and obtained a value for the width which agrees within 6% with our empirical value.

TABLE II. Numbers of triangles with sides $a=1$, b, c occurring in f.c.c and hcp lattices.

No.	b^2	c^2	N_{hcp}	N_{fcc}
1	1	1	24	24
2	1	2	36	36
3	1	$2\frac{2}{3}$	9	0
4	1	3	54	72
5	1	$3\frac{2}{3}$	18	0
6	1	4	9	18
7	2	3	36	48
8	2	$3\frac{2}{3}$	24	0
9	2	5	24	48
10	2	$5\frac{2}{3}$	12	0
11	$2\frac{2}{3}$	$3\frac{2}{3}$	24	0
12	$2\frac{2}{3}$	$6\frac{1}{3}$	12	0
13	3	3	36	48
14	3	$3\frac{2}{3}$	24	0
15	3	4	48	96
16	3	5	48	96
17	3	$5\frac{2}{3}$	24	0
18	3	6	36	48
19	3	$6\frac{2}{3}$	24	0
20	3	7	48	96
21	$3\frac{2}{3}$	$3\frac{2}{3}$	24	0
22	$3\frac{2}{3}$	$5\frac{2}{3}$	48	0
23	$3\frac{2}{3}$	$6\frac{1}{3}$	24	0
24	$3\frac{2}{3}$	$6\frac{2}{3}$	24	0
25	$3\frac{2}{3}$	$7\frac{1}{3}$	24	0
26	$3\frac{2}{3}$	$8\frac{1}{3}$	24	0
27	4	5	24	48
28	4	7	48	96
29	4	9	12	24
30	5	5	12	48
31	5	$5\frac{2}{3}$	24	0
32	5	$6\frac{2}{3}$	24	0
33	5	7	48	96
34	5	8	0	48
35	5	9	24	96
36	5	$9\frac{2}{3}$	24	0
37	5	10	24	48
38	$5\frac{2}{3}$	6	12	0
39	$5\frac{2}{3}$	$6\frac{2}{3}$	48	0
40	$5\frac{2}{3}$	$7\frac{1}{3}$	12	0
41	$5\frac{2}{3}$	$8\frac{1}{3}$	24	0
42	$5\frac{2}{3}$	$9\frac{2}{3}$	48	0
43	$5\frac{2}{3}$	$10\frac{1}{3}$	24	0
44	$5\frac{2}{3}$	$11\frac{1}{3}$	12	0
45	6	7	48	96
46	6	$9\frac{2}{3}$	24	0
47	6	11	24	48
48	$6\frac{1}{3}$	$6\frac{1}{3}$	12	0
49	$6\frac{1}{3}$	$7\frac{1}{3}$	24	0
50	$6\frac{1}{3}$	$8\frac{1}{3}$	24	0
51	$6\frac{1}{3}$	$10\frac{2}{3}$	12	0
52	$6\frac{1}{3}$	$11\frac{2}{3}$	24	0
53	$6\frac{2}{3}$	7	24	0
54	$6\frac{2}{3}$	$8\frac{1}{3}$	24	0
55	$6\frac{2}{3}$	$9\frac{2}{3}$	48	0
56	$6\frac{2}{3}$	$10\frac{1}{3}$	24	0
57	$6\frac{2}{3}$	$11\frac{2}{3}$	24	0
58	$6\frac{2}{3}$	$12\frac{1}{3}$	24	0
59	7	7	36	96
60	7	9	72	192
61	7	$9\frac{2}{3}$	24	0
62	7	10	48	96
63	7	11	48	96
64	7	$11\frac{2}{3}$	24	0
65	7	12	24	96
66	7	13	48	96
67	$7\frac{1}{3}$	$8\frac{1}{3}$	24	0
68	$7\frac{1}{3}$	$10\frac{1}{3}$	24	0
69	$7\frac{1}{3}$	$11\frac{2}{3}$	24	0
70	$7\frac{1}{3}$	$13\frac{2}{3}$	12	0
71	8	9	0	48
72	8	13	0	48
73	$8\frac{1}{3}$	$8\frac{1}{3}$	12	0
74	$8\frac{1}{3}$	$10\frac{1}{3}$	24	0
75	$8\frac{1}{3}$	$11\frac{1}{3}$	24	0
76	$8\frac{1}{3}$	$11\frac{2}{3}$	24	0
77	$8\frac{1}{3}$	$12\frac{1}{3}$	24	0
78	$8\frac{1}{3}$	$13\frac{2}{3}$	24	0
79	$8\frac{1}{3}$	$14\frac{2}{3}$	24	0
80	9	$9\frac{2}{3}$	24	0
81	9	10	48	144
82	9	12	12	48
83	9	13	48	192
84	9	$14\frac{2}{3}$	12	0
85	9	15	24	96
86	9	16	12	24
87	$9\frac{2}{3}$	$9\frac{2}{3}$	24	0
88	$9\frac{2}{3}$	10	24	0
89	$9\frac{2}{3}$	$10\frac{1}{3}$	24	0
90	$9\frac{2}{3}$	11	24	0
91	$9\frac{2}{3}$	$11\frac{1}{3}$	24	0
92	$9\frac{2}{3}$	$11\frac{2}{3}$	48	0
93	$9\frac{2}{3}$	$12\frac{1}{3}$	24	0
94	$9\frac{2}{3}$	$14\frac{1}{3}$	24	0
95	$9\frac{2}{3}$	$14\frac{2}{3}$	48	0
96	$9\frac{2}{3}$	$15\frac{1}{3}$	24	0
97	$9\frac{2}{3}$	$15\frac{2}{3}$	48	0
98	$9\frac{2}{3}$	$16\frac{1}{3}$	24	0
99	10	$11\frac{2}{3}$	24	0
100	10	13	48	144
101	10	15	24	96
102	10	$15\frac{2}{3}$	24	0
103	10	17	24	48
104	$10\frac{1}{3}$	$10\frac{1}{3}$	12	0
105	$10\frac{1}{3}$	$12\frac{1}{3}$	24	0
106	$10\frac{1}{3}$	$13\frac{2}{3}$	24	0
107	$10\frac{1}{3}$	$14\frac{1}{3}$	24	0
108	$10\frac{1}{3}$	$14\frac{2}{3}$	24	0
109	$10\frac{1}{3}$	$15\frac{1}{3}$	24	0
110	$10\frac{2}{3}$	$17\frac{2}{3}$	24	0
111	11	11	12	48
112	11	12	24	96
113	11	13	48	96
114	11	$14\frac{2}{3}$	24	0
115	11	$15\frac{2}{3}$	24	0
116	11	17	24	96
117	11	18	24	48
118	$11\frac{1}{3}$	$12\frac{1}{3}$	24	0
119	$11\frac{1}{3}$	$13\frac{2}{3}$	12	0
120	$11\frac{1}{3}$	$16\frac{1}{3}$	24	0
121	$11\frac{1}{3}$	$17\frac{2}{3}$	24	0
122	$11\frac{2}{3}$	$10\frac{2}{3}$	24	0
123	$11\frac{2}{3}$	$11\frac{2}{3}$	24	0
124	$11\frac{2}{3}$	$12\frac{1}{3}$	24	0
125	$11\frac{2}{3}$	13	24	0
126	$11\frac{2}{3}$	$13\frac{2}{3}$	48	0
127	$11\frac{2}{3}$	$14\frac{2}{3}$	24	0
128	$11\frac{2}{3}$	$15\frac{1}{3}$	24	0
129	$11\frac{2}{3}$	$15\frac{2}{3}$	48	0
130	$11\frac{2}{3}$	17	24	0
131	$11\frac{2}{3}$	18	24	0
132	$11\frac{2}{3}$	$18\frac{1}{3}$	24	0
133	$11\frac{2}{3}$	$18\frac{2}{3}$	24	0
134	$11\frac{2}{3}$	19	24	0
135	12	13	24	96
136	12	15	24	96
137	12	17	12	48
138	12	19	24	96
139	$12\frac{1}{3}$	$14\frac{2}{3}$	24	0
140	$12\frac{1}{3}$	$15\frac{1}{3}$	24	0
141	$12\frac{1}{3}$	$16\frac{1}{3}$	24	0
142	$12\frac{1}{3}$	$17\frac{2}{3}$	24	0
143	$12\frac{1}{3}$	$18\frac{1}{3}$	24	0
144	$12\frac{1}{3}$	$19\frac{2}{3}$	24	0
145	13	13	24	96
146	13	15	24	192
147	13	$15\frac{2}{3}$	24	0

ments of $(H'^2)_{00}$ are evaluated in the same way as for the dipole-dipole interactions. The calculations are straightforward and give the following result for a particular triangle for the relative deviation:

$$\left[\frac{W''-W_0''}{W_0''(ABC)}\right]_{d-q}=-\left(\frac{\Delta^2}{1-\Delta^2}\right)\left\{\frac{1}{R_{AB}{}^8}+\frac{1}{R_{AC}{}^8}+\frac{1}{R_{BC}{}^8}\right\}^{-1}$$

$$\times\left\{\frac{1}{R_{AC}{}^8}\left[\tfrac{3}{5}\mu^2(1+2\cos^2\gamma_1)\right.\right.$$

$$\left.+\tfrac{1}{10}\mu^4(1-2\cos^2\gamma_1+5\cos^4\gamma_1)\right]$$

$$+\frac{1}{R_{BC}{}^8}\left[\tfrac{3}{5}\mu^2(1+2\cos^2\gamma_2)\right.$$

$$\left.+\tfrac{1}{10}\mu^4(1-2\cos^2\gamma_2+5\cos^4\gamma_2)\right]$$

$$+\frac{\mu^2}{5R_{AC}{}^4R_{BC}{}^4}\left[2(1-2\cos^2\gamma_3)\sin\gamma_1\sin\gamma_2\right.$$

$$+6\sin^2\gamma_3\cos^2\gamma_3-3(1-3\cos^2\gamma_3)\cos\gamma_1\cos\gamma_2$$

$$+\mu^2(\cos\gamma_3\{1-3\cos^2\gamma_1-3\cos^2\gamma_2$$

$$-4\sin\gamma_1\cos\gamma_1\sin\gamma_2\cos\gamma_2+9\cos^2\gamma_1\cos^2\gamma_2\}$$

$$-\sin\gamma_3\{2\sin\gamma_1\cos\gamma_1+2\sin\gamma_2\cos\gamma_2$$

$$\left.\left.-6\cos\gamma_1\cos\gamma_2\sin\gamma_3\})\right]\right\}.$$

In principle, higher multipole interactions can be found in a similar manner, but the calculations become very tedious. Since we are primarily interested in the order of magnitude of three-body forces, we shall not carry the computations further.

SUMMATION OVER CRYSTAL STRUCTURES

The expressions obtained for the three-body dipole-dipole and dipole-quadrupole forces must now be summed over the hexagonal and cubic close-packed lattices to determine which is more stable. We consider only triangles in which one side (R_{AB}) is a nearest-neighbor distance in the crystals. We need a list of all such triangles appearing in the crystals and a count of how many of each kind there are in each lattice.

The face-centered cubic and hexagonal close-packed lattices can be formed by stacking layers of hexagonally arrayed atoms. Consider a Cartesian coordinate system with the x-y plane in a hexagonal layer such that the x-axis passes through nearest neighbors. We will call this an A layer. We can construct layers B and C by shifting an A layer a distance $r_0/\sqrt{3}$ and $-r_0/\sqrt{3}$ in the y direction, respectively. The sequence of layers in the fcc lattice is then $ABCABC\cdots$, and in the hcp lattice it is $ABABAB\cdots$. A convenient way to count triangles in these lattices has been devised by Axilrod.[7] We will summarize the results briefly. The sides a, b, c

of a particular triangle in either lattice are given by

$$\begin{aligned} a^2 &= (n_1-\tfrac{1}{2}n_2)^2+\tfrac{3}{4}(n_2+\tfrac{2}{3}N_3)^2+\tfrac{2}{3}n_3^2, \\ b^2 &= (m_1-\tfrac{1}{2}m_2)^2+\tfrac{3}{4}(m_2+\tfrac{2}{3}M_3)^2+\tfrac{2}{3}m_3^2, \\ c^2 &= a^2+b^2-2(n_1-\tfrac{1}{2}n_2)(m_1-\tfrac{1}{2}m_2) \\ &\quad -\tfrac{3}{2}(n_2+\tfrac{2}{3}N_3)(m_2+\tfrac{2}{3}M_3)-(4/3)n_3m_3, \end{aligned} \tag{12}$$

where each n_i and m_j assumes all integral values. The integers N_3 and M_3 are defined as follows:

(1) In the hcp lattice: N_3 is zero or one when n_3 is even or odd with a similar dependence of M_3 on m_3.

(2) For the f.c.c lattice: $N_3=0$ for $n_3=3s$, $N_3=1$ for $n_3=3s+1$, and $N_3=-1$ for $n_3=3s+2$, where s is an integer; M_3 depends on m_3 in a similar manner.

The triangles are counted within a region distance $r_0\sqrt{15}$ from the origin. Table II gives the numbers of triangles of different types in each of the two lattices; $a^2=1$ for all of the triangles. With the help of this table, we can calculate the ratio $\sum(W''-W_0'')/\sum W_0''$ for each lattice for both the three-body dipole-dipole and the three-body dipole-quadrupole interactions. Since the theory is not applicable if atom C is close to either A or B, we will discard triangles in which C is a nearest neighbor of either A or B (No. 1 through No. 6). The total number of triangles in the region of summation is approximately 3600, of which 141 are different (No. 7 through No. 147). Since the sign of the difference between the two lattices appears to be critically dependent on the distance of closest approach of atom C, we computed three different results. The first includes all the different kinds of triangles from 7 through 147. For the second sum we deleted the smallest triangle with sides squared 1, 2, 3, and in the third case we deleted all triangles for which b^2 or c^2 is 2. Table III gives these results. Each partial summation extends over the same number of triangles in each lattice. Even after summing over 3600 triangles, the result is not converging rapidly; however, it is found that after the first 39 different triangles (No. 7 through No. 46), the difference between the sums for the two lattices is practically constant.

The total relative magnitude of the three-body forces is found from the following formula:

$$\frac{\sum(W''-W_0'')_{d-d}+(f_2/f_1)\sum(W''-W_0'')_{d-q}}{(\sum W_0'')_{d-d}+(f_2/f_1)(\sum W_0'')_{d-q}}, \tag{13}$$

where

$$f_1=\frac{3e^4}{4E_{\text{Av}}\beta^4r_0^6},\quad f_2=\frac{45e^4}{8E_{\text{Av}}\beta^6r_0^8},$$

and, therefore,

$$f_2/f_1=15/8\mu^2. \tag{14}$$

The nearest-neighbor distance in the crystal is r_0, and $\mu=\beta r_0/2$. The values of f_2/f_1 are 0.634, 1.31, 1.71, and 1.90 for neon, argon, krypton, and xenon, respectively. If a three-dimensional harmonic-oscillator model with a single charge is used for the atom, then f_2/f_1 is $5/4\mu^2$.§ Therefore, the Gaussian wave function emphasizes the higher multipole contributions more than does the harmonic oscillator model; this tendency continues in the case of quadrupole-quadrupole interactions. In either model, however, the quadrupole-quadrupole forces contribute less to the cohesive energy than the dipole-quadrupole forces. The numerical results for Eq. (13) are given in Table IV.

TABLE III. Relative magnitude of three-body dipole-dipole and dipole-quadrupole interactions in the f.c.c. and hcp lattices: $\Sigma(W''-W_0'')/\Sigma W_0''$.

Region of summation	Element	Dipole-dipole			Dipole-quadrupole		
		f.c.c.	hcp	Diff. ×10²	f.c.c.	hcp	Diff. ×10²
7–147	Ne	0.00886	0.00879	0.007	0.0134	0.0135	−0.01
	A	0.0962	0.0955	0.07	0.126	0.127	−0.1
	Kr	0.152	0.151	0.1	0.193	0.194	−0.1
	Xe	0.177	0.175	0.2	0.221	0.222	−0.1
8–147	Ne	0.00709	0.00718	−0.009	0.0106	0.0108	−0.02
	A	0.0771	0.0780	−0.09	0.101	0.102	−0.1
	Kr	0.122	0.123	−0.1	0.155	0.157	−0.2
	Xe	0.141	0.143	−0.2	0.178	0.180	−0.2
11–147	Ne	0.00548	0.00545	0.003	0.00748	0.00747	0.001
	A	0.0596	0.0592	0.04	0.0703	0.0702	0.01
	Kr	0.0941	0.0935	0.06	0.107	0.107	0
	Xe	0.109	0.109	0	0.123	0.123	0

DISCUSSION

We conclude from this analysis that three-body long-range forces contribute significantly to the static lattice energy of crystals of the heavy rare gases. The use of two-body potentials to describe physical properties of dense media is based on the assumption of point molecules. In our formalism this means that β approaches infinity and the Gaussian becomes a Dirac δ function. This assumption becomes more invalid the larger the molecules and the denser the medium. (The same conclusion holds for Axilrod's third-order effect in which

TABLE IV. Relative total magnitude of three-body forces in the f.c.c. and hcp lattices.

Region of summation	Element	f_2/f_1	f.c.c.	hcp	(f.c.c.-hcp) ×10
7–147	Ne	0.634	0.0105	0.0105	0
	A	1.31	0.112	0.112	0
	Kr	1.71	0.177	0.177	0
	Xe	1.90	0.205	0.205	0
8–147	Ne	0.634	0.00836	0.00850	−0.014
	A	1.31	0.0900	0.0912	−0.12
	Kr	1.71	0.142	0.143	−0.1
	Xe	1.90	0.164	0.166	−0.2
11–147	Ne	0.634	0.00620	0.00618	0.002
	A	1.31	0.0653	0.0651	0.02
	Kr	1.71	0.102	0.102	0
	Xe	1.90	0.118	0.118	0

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§ H. Margenau, Revs. Modern Phys. **11**, 1 (1939). The reason that f_2/f_1 is different in our model from that of harmonic oscillators is primarily that the energy levels of harmonic oscillators are equally spaced while we have used a centroid assumption.

the parameter determining the magnitude of the triple-dipole energy is α/r_0^3, with the polarizability α becoming larger for larger molecules.[7]) It is, therefore, not surprising that different forms for two-body potentials are found from analysis of different physical phenomena. It appears that in molecular physics the occurrence of many-body forces is a direct consequence of the fact that atoms and molecules are not "fundamental" (or "point") particles.

Some conclusions may also be drawn with respect to the stability of rare gas crystals. Since the calculations apply to the static lattice energy, we assume that the crystal structures are still cubic at 0°K. The data available at the lowest temperature are for neon which has been measured at 4 °K.[13] The possibility of a thermal transition to the hexagonal structure below this temperature can be eliminated on the basis of Domb and Barron's analysis.[4] We also assume that the difference in zero-point energy between the two crystal structures is negligible; this has been verified theoretically for pair-potential functions.[14,4] However, in view of the importance of three-body forces, this conclusion should be substantiated by extending the Born-von Kármán lattice dynamics theory to include many-body interactions.[15]

The results in Tables III and IV indicate that the difference in three-body forces between the two lattices depends markedly on the distance of closest approach of atom C. If all the triangles 1 through 147 are included in the summation, the result is a very large repulsive energy. The theory, however, is not strictly valid for triangles with two or three nearest neighbors; so, these results have not been listed in the tables. Nevertheless, their size shows how sensitive three-body forces are to the exact nature of the model used, and this in turn implies that using an approximate model (e.g., harmonic oscillators) and extending the calculations to nearest neighbors in the crystal is unjustified. It may be remarked that for Axilrod's third-order dipole-dipole energy the triangles with two or three nearest neighbors contribute more than half of the three-body interactions and half of the difference between the two crystal structures.[7] Summing over triangles 8 through 147 gives a result which is definitely in favor of the fcc lattice both for dipole-dipole and dipole-quadrupole interactions, the difference being of the order of one tenth of one percent of the van der Waals energy of the crystal. *This difference is an order of magnitude larger than that obtained on the basis of pair potentials*, and it is of opposite sign. If the three-body forces do not affect the sign of the difference between the Debye characteristic temperatures of the two crystals,[4] then this would mean that the cubic structure is stable at all temperatures. However, the difference between the two crystals becomes indecisive if the summations are carried out over triangles 7 through 147 or 11 through 147. Even if atom C is restricted to a region which is relatively far from a central atom, multipoles of still higher order should be included in the calculation. In addition, one would have to account for triangular configurations with two or three nearest neighbors to which the present theory does not apply. We have shown that three-body forces in second-order perturbation theory may increase the difference in lattice energy between the two crystal structures by an order of magnitude compared with that based on the assumption of two-body forces.

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[13] de Smedt, Keesom, and Mooy, Proc. Acad. Sci. Amsterdam **33**, 255 (1930).

[14] L. Jansen and J. M. Dawson, J. Chem. Phys. **23**, 482 (1955).

[15] An additional condition, of course, is that the cubic crystal structure is really the equilibrium configuration and not a frozen-in unstable state.