63-3-4

[redacted]

Battelle

centre de recherche de Genève

160718

BATTELLE MEMORIAL INSTITUTE
International Division
7, route de Drize
Geneva

Final Technical Report
(January 31, 1963)

SOLID-STATE PROPERTIES OF NON-CONDUCTING MATERIALS OF SIMPLE MONATOMIC AND DIATOMIC SPECIES

by

Laurens Jansen, Samson Zimering
and Michael H. Boon

for

EUROPEAN RESEARCH OFFICE (9851 DU)
U. S. Department of the Army
Frankfurt/Main, Germany
APO 757, U. S. Forces

Contract number : DA-91-591 - EUC-2071
Period : December 1, 1961 - November 30, 1962

The research reported in this document has been made possible through the support and sponsorship of the U. S. Department of Army, through its European Research Office.

ABSTRACT

During the second year of research under the above contract the analysis of the problem concerning the stability of crystal structures for the heavy rare gas atoms has been completed. There exists firm experimental evidence that neon, argon, krypton and xenon crystallize in the face-centered cubic (fcc) structure, whereas helium, under pressure, forms crystals of hexagonal closest packing (hcp). According to calculations based on pair-potentials, however, the hexagonal lattice should be somewhat more stable for all rare gas solids involved.

This problem, which was discussed in detail for the first time in the literature exactly twenty years ago (B. M. Axilrod and E. Teller, J. Chem. Phys. 11, 299 (1943)), received much increased attention since about 1955. A satisfactory solution, which would at the same time constitute the first absolute stability proof for any crystalline structure, had, however, so far not been found.

The underlying hypothesis for the analysis of this important problem under the present contract was that the fcc-structure becomes the more stable one if deviations from the principle of pair-potentials between the atoms are taken into account. Since, in principle, there occur many possible types of such manybody interactions, a systematic analysis of these various effects was undertaken during the first year of the contract, based on an exchange cluster expansion and making use of a perturbation treatment (L. Jansen, Phys. Rev. 125, 1798 (1962); Special Technical and Scientific Report No 2, July 31, 1961).

First-order calculations were carried out during the first year (see above references); the second year was devoted to the evaluation of second-order threebody interactions between rare gas atoms, and to an application of the results in first and second orders to the stability problem of rare gas solids.

To avoid difficulties of convergence with the use of a multipole expansion for the electrostatic interactions between the atoms, the integrals were evaluated with the perturbation terms in unexpanded form. Instead, for the present type of problem it was found possible to use a Gaussian-effective-electron model, in which a single parameter characterizes the rare gas atom considered.

Since the first- and second-order threebody interactions are of very short range, the analysis was limited to triangles formed by a central atom in each lattice and two of its twelve nearest neighbors. There exist 66 of such triangles for each lattice, 57 of which are the same between the two structures, whereas 9 are different.

It appeared during the analysis that the occurring many integrals of second order (direct and exchange integrals, many of which are of a three-center type) lead to long and complex mathematical problems for their evaluation. The formal expressions, being considerably more complicated than those occurring in first order, require high numerical precision to render the final result reliable. First essays, with electronic computation, proved much too costly and not sufficiently accurate for this type of problem. .

It was therefore necessary to look for special methods, based on integral-transformation followed by asymptotic series expansions. Fortunately, and to our surprise, it appeared possible to find excellent asymptotic expansions for the five basic integral types involved in the problem. The precision attained in this way was much more satisfactory than that given by electronic computation, especially for large values of the variables.

In this way, it was possible to evaluate the final result with required precision and to express it in analytic form; the expression is of the type of a sum of exponentially decreasing functions of the three sides of the triangle considered, plus a sum of inverse powers of these distances.

We considered, as in the first-order calculations, the nine different triangles among the sixty-six in each lattice, formed by a central atom and two of its twelve nearest neighbors. The results can be expressed in terms of the dimensionless parameter βR, where β is the characteristic parameter of the Gaussian charge distribution, and R the nearest-neighbor distance in the lattice, and the angle θ between the two sides of the triangle which originate at the central atom.

Detailed results for argon were obtained for $\theta = 60^{o}$, and for the critical 120^{o}- and 180^{o}-configurations of the fcc-structure; approximate values were already determined for the other important triangles $\theta = 110^{o}$ and $\theta = 146^{o}$ of the hcp-lattice. In addition, the behavior of the relative second-order threebody component, $\Delta E_2/E_2^{(o)}$, where ΔE_2 is the three-body contribution, $E_2^{(o)}$ the pair-potential second-order energy for the atoms on the triangle, as a function of θ for the other heavy rare gas atoms was established.

The first-order results, obtained previously, were then reexpressed in terms of θ and βR for the same triangles, and the corresponding relative first-order threebody component $\Delta E_1/E_1^{(o)}$ compared with its analogue in second order. The sensational result of this comparison is that the curves for $\Delta E_1/E_1^{(o)}$ and $\Delta E_2/E_2^{(o)}$ are practically one and the same function; for argon it starts at -20 percent for $\theta = 60^{o}$, increases very rapidly until $\theta \approx 120^{o}$ and is almost constant from $\theta = 120^{o}$ to $\theta = 180^{o}$.

We have also demonstrated that this type of curve is unambiguously in favor of the hcp-lattice as far as $\Delta E_1/E_1^{(o)}$ is concerned. On the other hand, the curve stabilizes the fcc-lattice in second order, since the denominator $E_2^{(o)}$ is negative. Since the lattice energy itself is a negative quantity, the resulting curve favors the face-centered cubic configuration. A more accurate comparison for the types of triangles mentioned above yielded $\Delta E_2 \approx -2 \Delta E_1$, which is, remarkably enough, just the same ratio as there exists between $E_2^{(o)}$ and $E_1^{(o)}$.

This effect has some of the general characteristics of the Teller-Axilrod triple-dipole (third-order) contribution, but it gives rise to a much larger difference between the fcc- and hcp-structures. The large difference derives from the very special behavior of the $\Delta E_1/E_1^{(o)}$- or $\Delta E_2/E_2^{(o)}$-curve in the neighborhood of $\theta = 110^{o}$ to $\theta = 120^{o}$.

In addition to explaining the stability of the face-centered cubic configuration for solids of the heavy rare gases, the theory predicts, in particular, that the interaction between atoms in an equilateral triangular array will be 20 percent less negative than the sum of its pair-potentials. In this connection, a very recent investigation of the specific heat of solid argon (at constant volume) by Foreman and Lidiard (Phil. Mag., in the press) is of great interest. For their calculation, these authors used the anharmonic Einstein model; from the results they estimated the free energy of formation of a vacancy. There is a discrepancy between these results and experimental values. Foreman and Lidiard suggest after careful analysis that the discrepancy can be due to the effect of threebody interactions and estimate a relative effect of about -25 percent for an equilateral triangle of argon atoms. Our theoretical result is in agreement with their estimate.

It may possibly also be anticipated that the unexplained difference in crystal structures occurring among the alkali halides (for example, NaCl and KCl on one hand, CsCl on the other hand) will find a similar explanation. We note that the corresponding ions are isoelectronic with the rare gas atoms. Preliminary investigations are in progress on this subject.

We have also initiated a band theoretical calculation for the same problem, in which the influence of symmetry on the positions and multiplicities of the s- and p-bands of solid argon in the fcc- and hcp-configurations is studied. In this analysis, extensive use is made of group-theoretical considerations. Again, the first result has been that the difference in lattice energy between the two configurations must be due to the effect of manybody interactions. The various threebody terms, which are now of the type

$$\int u^*_i(r)\, V(r - R_\nu)\, u_j\, (r - R\mu)\, d\tau \;,$$

where u_i, u_j denote 3s- or 3p-functions, $V(r - R_\nu)$ the atomic potential of an atom with nucleus centered at R_ν, and where $\mu \neq \nu$, and $\mu, \nu \neq 0$, are being evaluated.

This component of the research must be seen in connection with the general problem concerning the effect of (slight) changes in symmetry of a solid system on its band structure; the analysis is being undertaken in conjunction with a different project. Results have already been obtained for a slightly distorted fcc-lattice (2 atoms per unit cell instead of one); it is envisaged that also the influence of deviations from the ideal c/a-ratio in fcc-lattices, deviations which normally occur in nature, on the band structure of molecular solids will be analyzed.

OUTLINE OF RESEARCH PROJECT

Concerning properties of materials in general, it is nowadays recognized that no essential progress is possible without extensive fundamental research. In the past, most of the theoretical investigations in the field of properties of solid materials have been directed towards an explanation of phenomena associated with metallic substances, of semi-conductors, and, to a lesser extent, of ionic crystals. Compared with this group of materials, the theory of molecular solids (insulators) has received but little attention, and even the most striking facts exhibited by such materials often lack a satisfactory explanation. It has become more and more urgent to try to fill this gap, since molecular solids have become of increasing importance also from a practical point of view. As an example it might be mentioned that the stability of the close-packed cubic crystal structure of the heavy rare gases (neon, argon, krypton and xenon) cannot be explained on the basis of existing theories. One finds that the hexagonal close-packed crystal form (the helium structure) should be more stable than the cubic structure, and this result is remarkably insensitive with respect to the precise form of intermolecular potentials. Concerning this problem the present investigator has suggested that an explanation may be found on the basis of the effect of manybody forces of the van der Waals-type (second-order of perturbation theory) on the stability. Preliminary calculations have shown that this explanation may be the correct one, and that present theories of molecular solids need considerable modification.

The crystals of nitrogen and carbon monoxide are also cubic close-packed at the lowest temperatures, but show a transition to the hexagonal closest packing at $35^{\circ}K$ and $61^{\circ}K$, respectively. The present investigator has suggested that the stability of these crystals and the transition mechanism may involve orientational interactions (e. g. those due to permanent electric quadrupole moments) in the solids. The cubic structure is favored by quadrupole interactions in the solids, whereas the hexagonal structure is preferred by anisotropic components of the van der Waals forces. As the temperature increases and herewith the rotational amplitudes of the molecular axes, the quadrupole forces, being of first order, die out much more quickly that the (second-order) van der Waals forces. The results obtained so far suggest strongly that this explanation may be the correct one, although a quantitative theory is still lacking.

Molecular solids have recently become of importance also as materials in which free radicals can be trapped and stored. The results obtained in this field provide an invaluable experimental background for the development of a crystal field theory of molecular solids. This investigator has been associated with the Free Radicals Research Group at the National Bureau of Standards in Washington, D.C., and has performed some preliminary calculations which seem to indicate that present theories of molecular solids are in need of substantial improvement in order to yield satisfactory agreement with experimental data.

SUMMARY OF RESULTS OBTAINED DURING SECOND YEAR

The results obtained during the second year under the project may be divided into three categories:

I. Completion of the analysis concerning absolute stability of the cubic configurations of heavy rare gas solids, following the general classification of manybody interactions developed during the first year (Phys. Rev. 125, 1798 (1962)). The theory cannot only explain this stability, it is also in agreement with recent experimental results concerning the free energy of formation of a vacancy in solid argon (A. J. E. Foreman and A. B. Lidiard, Phil. Mag., in the press).

Two manuscripts containing the results of this investigation ("Absolute Stability of Cubic Crystal Structures of Heavy Rare Gas Atoms" I and II) will be submitted for publication in Physics Letters before February 1. Their texts are given in original form in the following section ANALYSIS OF RESEARCH PERFORMED of this Report.

II. Development of asymptotic series expansions for integrals of three-center type. The corresponding methods and results for various triangular configurations of rare gas atoms will be published elsewhere and also prepared for the Special Technical and Scientific Report No. 6.

III. A band theoretical analysis of the argon stability problem. We await here the evaluation of three-center integrals. Dr Michael H. Boon is conducting this part of the research, in collaboration with Dr Erminio Lombardi, a guest from the Institute of Technology, Milano, Italy. Although Dr Lombardi is engaged in research under the project, his expenditures are covered by independent sources.

A Special Technical and Scientific Report No. 5 (May 31, 1962) was issued containing some preliminary results on the evaluation of three-center integrals.

ANALYSIS OF RESEARCH PERFORMED

GENERAL

The following sections contain a discussion of results obtained on the problem of stability of crystals of the heavy rare gas atoms. For simplicity, the texts of two manuscripts with the title ABSOLUTE STABILITY OF CUBIC CRYSTAL STRUCTURES OF HEAVY RARE GAS ATOMS, I and II, are given in their original forms, whereby the page-numbering of these manuscripts has been retained. The texts have been prepared for publication in Physics Letters (Amsterdam), since it was felt that the results warrant quick publication.

Since the band theoretical analysis of the stability problem for solid argon has not yet been completed, the results obtained so far on this part of the research are not included in this Report.

A brief discussion of the results on the stability problem has been presented in the first section of the present Report; we will, therefore, not abstract these results here.

ABSOLUTE STABILITY OF CUBIC CRYSTAL STRUCTURES OF HEAVY RARE GAS ATOMS I*

Laurens Jansen
Battelle Memorial Institute, International Division,
Geneva, Switzerland

(Received)

Twenty years ago$^{1)}$ the problem concerning the absolute stability of the observed face-centered cubic crystal structures of neon, argon, krypton and xenon was for the first time discussed in detail in the literature. In conjunction with the pioneering work by Born and collaborators$^{2)}$ on the mechanical stability of crystals, this also marked the first realistic attempt to provide an explanation for the absolute stability of any crystalline substance.

The problem arose since it was found that all other available experimental data on crystals of neon, argon, krypton and xenon could be explained in a satisfactory manner on the basis of pair-potentials between the atoms. However, the static lattice energy, written as a sum of interactions between pairs of atoms, favors the hexagonal close-packed (hcp) structure instead of the experimentally found face-centered cubic (fcc) configuration. The difference in energy between these two lattices is very small, only of the order of one hundredth of one percent, but is remarkably stable with respect to admissible changes in the potential between two atoms$^{3)-7)}$.

---

* This research has been made possible through the support and sponsorship of the U.S. Department of Army, through its European Research Office.

Careful considerations of the influence of zero-point energy[7][8], and of the possibility for thermal transitions between the two structures by Barron and Domb[7] yielded the same negative results : the hcp-structure is somewhat more stable than the fcc-configuration. Only He^4, crystallizing under pressure in the hcp-structure, appeared to behave normally.

There are two categories of possible solutions for this problem :

a) the interactions between rare gas atoms contain non-negligible manybody components, i. e. the crystal energy cannot be written as an additive sum-over-pairs.

b) the interaction between two atoms is angular dependent.

Practically all proposed solutions have, explicitly or implicitly, been based on assumption a). Only Cuthbert and Linnett[9] suggested an explanation of type b) : according to calculations by Linnett and Pöe[10] the most probable configuration of the group of eight electrons in heavy rare gas atoms is as four pairs at the corners of a regular tetrahedron, the nucleus being at the center. This leads to an angular dependent electrostatic interaction between two such tetrahedra, which favors the cubic lattice. No quantitative results were obtained.

On the other hand, the presumedly very high stability of the closed-shell configurations of rare gas atoms led to the supposition that many-body interactions between such atoms could only be a higher-order perturbation effect (starting from third order), or that they could be important only at very small interatomic distances, where first-order interactions prevail[11]. The first attempt, by Axilrod[12], was a third-order perturbation calculation for three non-overlapping rare gas atoms, i. e. a straightforward extension of London's derivation for second-order dipole-dipole interactions. This so-called triple-dipole effect <u>decreases</u> the attraction, compared with an additive sum-over-pairs, for an equilateral configuration of atoms, and increases the attraction for a linear array. The net effect, summed over the hcp- and fcc-lattices, favors the cubic configuration, but its magnitude is too small to overcome the small pair-potential difference between the two structures.

First-order calculations for three helium atoms were carried out by P. Rosen13) and Shostak14). Although helium is of no direct interest as far as its crystal structure is concerned, the sign of this first-order threebody effect may be noted : repulsion between three atoms is weaker for an equilateral triangle, and stronger for a linear array, than that calculated on the basis of an additive sum-over-pairs, i. e. the relative first-order effect has the same sign as the third-order triple-dipole contribution.

A variety of different-type manybody interactions has further been reported in the literature, based partly on electrostatic effects, in which overlap of charge clouds is treated classically4)15)16), or based on the Drude-model of harmonic oscillators for the atoms17)-21) with dipole-interactions*.

Finally, it was shown by one of us and R. T. McGinnies22)23) that also second-order interactions (i. e. of the usual van der Waals-type) are not additive if exchange effects are taken into account. The calculations were carried out for dipole-dipole and dipole-quadrupole components; a tendency towards stabilisation of the face-centered cubic configuration was observed.

All effects discussed above suffer from one, or several, of three main defects which make them unsuitable as a key to the explanation of the observed stability of the face-centered cubic structures for neon, argon, krypton and xenon :

---

[*] We mention also that R. S. Mulliken has suggested that polarization forces of a "charge-transfer" type may have an effect on the stability of rare gas crystals. (R. S. Mulliken, "The Interaction of Electron Donors and Acceptors", Conference on "Quantum Mechanical Methods in Valence Theory", published by Office of Naval Research, Washington, D. C. Sept. 1951, p. 108.) To this author's knowledge the above suggestion has never been worked out.

1) they concern systems of little interest (helium);
2) overlap between neighboring charge clouds is either neglected or treated classically;
3) a multipole expansion is used for the electrostatic interactions.

At small distances between atoms (those between nearest neighbors in the crystal) the interactions are mainly of exchange-type. Further, the use of a multipole expansion for the electrostatic interactions becomes increasingly less accurate as the distances between the atoms decrease. In fact, such series usually do not converge at all[24)-26)]. Exchange effects normally reverse the sign of contributions based on classical models; since the sign of any effect is of decisive importance for stability considerations, critical errors may be introduced in electrostatic models.

To find a satisfactory solution for the stability problem a model should be designed which avoids the defects mentioned earlier, which is sufficiently simple for numerical calculations, which, on the other hand, retains the possibly important factors characterizing the problem. Such a model may be devised as follows. We note that stability of the fcc-structures is a phenomenon common to solid neon, argon, krypton and xenon. Therefore, the explanation can depend only on some general parameter characteristic for the wave functions of these atoms, not on the detailed analytic form of the wave functions. We have here the choice between deviation from spherical symmetry and the dimension of an atom, and we choose the latter parameter. With this choice, the hcp-structure is supposed to be the more stable one for point-atoms, and for those solids of spherical atoms for which the ratio between atomic dimension and nearest-neighbor distance is smaller than a certain critical value, to be determined. For heavier atoms the fcc-structure should become more and more stable.

Further simplifications may be made. Explicit second-order contributions of threebody interactions between (helium or) neon atoms showed[22)] that multiple exchange of electrons between the same two atoms is not important for solids of these atoms. In addition, coupling of inter- and intra-atomic exchange gives only a very small contribution to the threebody exchange energy. Since neon crystallizes already in the fcc-configuration, we conclude that also for the heavier atoms multiple exchange (between the same two atoms) and coupled exchange can be neglected.

We are now left with a sum (average) of single-exchange interactions between different atoms. This sum is replaced by an exchange interaction between effective electrons, one on each atom. The problem becomes thus formally the same as that concerning hydrogen atoms with parallel spins. A convenient choice for the charge distribution of an effective electron is a Gaussian function

$$\rho(r) = (\beta/\pi^{1/2})^3 \exp(-\beta^2 r^2),$$

where r is the distance from the effective electron to its nucleus and where β is a parameter which measures the width of the charge distribution. It is possible to determine the values of β empirically by calculating van der Waals interactions between two such Gaussian atoms and equating the result to the attractive part of an empirical potential function[23)].

The threebody effect will then depend only on the configuration of a specific triangle considered and on the value of the dimensionless parameter βR, where R is the nearest-neighbor distance between the atoms. For solid neon, argon, krypton and xenon we find $\beta R = 3.44$, 2.10 and 2.00, respectively. The energy of interaction is expressed in units βe^2; for argon, for example, we find that $\beta e^2 \approx 10\text{eV}$, i.e., somewhat smaller than its first ionization potential ($\beta = 0.623$ Å^{-1}; $R = 3.84$ Å). For solid helium we have $\beta R = 5.75$, but validity of a Gaussian model for this atom is very doubtful.

We should therefore find that above a certain critical value of βR the hcp-structure is favored, whereas below this value the fcc-lattice becomes the more stable configuration. To carry out the calculations, we note that the sublimation energy of rare gas crystals is of the order of one hundred times smaller than those of ionic crystals or of metals. A perturbation treatment is, therefore, appropriate, whereby it is supposed that only first- and second-order effects must be included.

It is further supposed, since exchange effects decrease very rapidly with interatomic distances, that the main effect which stabilizes the fcc-structure lies already in a study of the difference between triplet-interactions involving a central atom and any two of its twelve nearest neighbors in the two configurations. As far as pair-interactions are concerned the two structures are identical up to the third shell of neighbors. However, if triangular configurations are taken into account, then we count 66 possible triangles in each structure, formed by a central atom and two of its nearest neighbors. Of these 66 triangles, 57 are the same between the two lattices, but 9 are different. These 9 different triangles are listed in Table I below; a, b, and c denote the three sides of the triangle in units of nearest-neighbor distance. We also list values for the angle θ between the two sides originating at the central atom.

Table I: The nine different triangles a, b, c with $a = b = 1$, between the hcp- and fcc-structures.

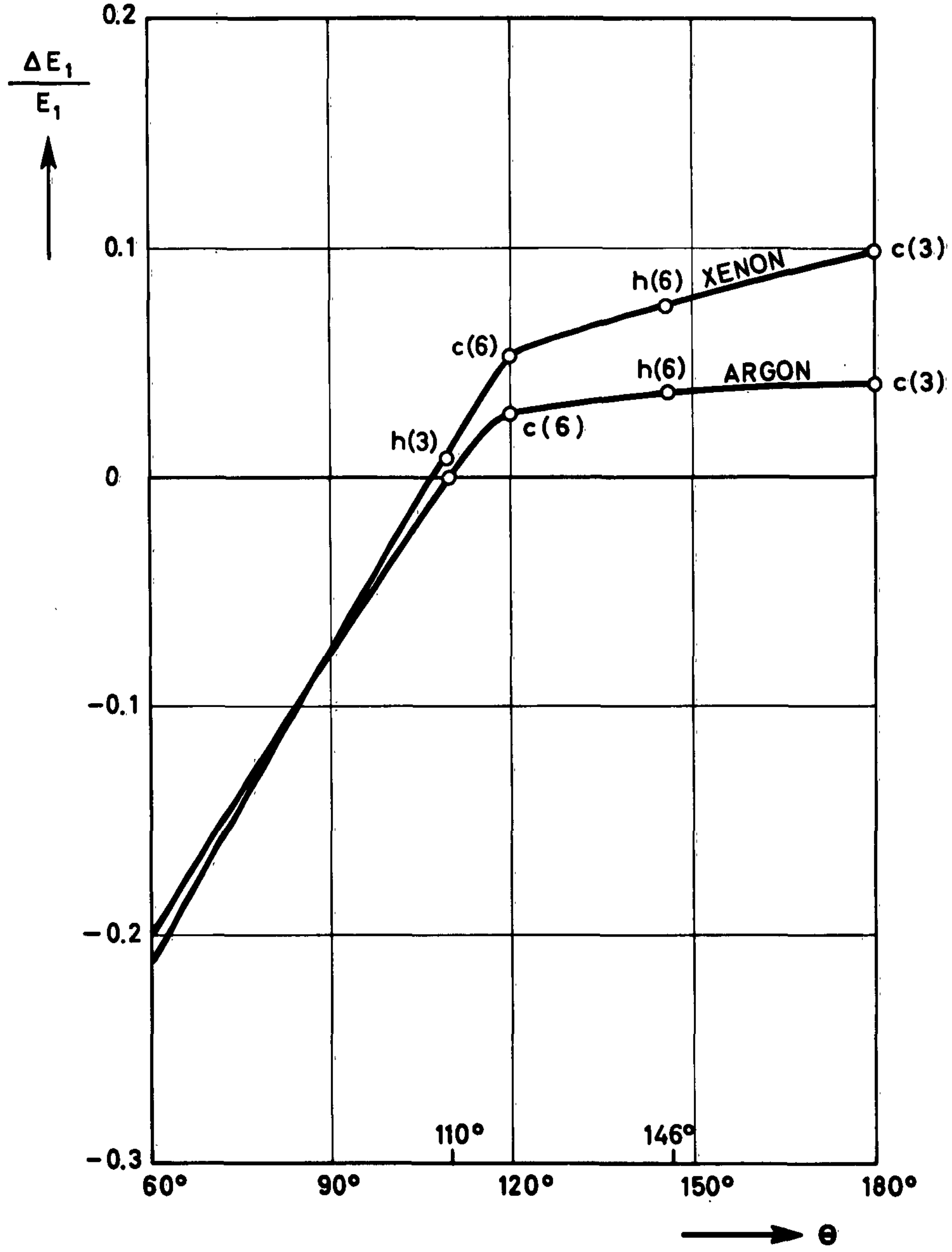
	a^2, b^2, c^2	θ	No	a^2, b^2, c^2	θ	No
h c p	1, 1, 8/3	110°	3	1, 1, 11/3	146°	6
f c c	1, 1, 3	120°	6	1, 1, 4	180°	3

These different triangles are all formed by a central atom, one atom on a triangle above the horizontal hexagonal layer, and one atom on a triangle below this layer. Corresponding atoms on the triangles above and below are just above each other in the hcp-lattice; in the fcc-configuration one of the triangles is rotated through 60° about the axis through its center and perpendicular to the horizontal plane.

A perturbation calculation is now carried out in first and second orders for the interaction energy between three Gaussian atoms in a specific triangular configuration. Different values of the parameter β represent the different rare gas atoms. The use of a multipole expansion is avoided by retaining the electrostatic interactions in their exact form.

First-order calculation. The correction to first-order (repulsive) interactions between three atoms in different triangular configurations has been published recently[27)]. These values have been supplemented by calculating also the correction for the critical 110°- and 146°-triangles of the hcp-lattice. The result is (cf. Fig. 1 of ref. 27) that the 146°-curve, as a function of βR, lies about half-way between the 120°- and 180°-curves, and that the effect for a 110°-configuration is very nearly zero, independent of the value for βR. In the following Fig. 1 we plot the relative threebody component of the first-order energy, $\Delta E_1/E_1$, as a function of the angle θ, for argon ($\beta R = 2.4$) and xenon ($\beta R = 2.0$). Note that the sign of this effect is the same as that found for three helium atoms by P. Rosen[13)] and Shostak[14)].

(Fig. 1)



$\frac{\Delta E_1}{E_1}$
0.2
0.1
0
−0.1
−0.2
−0.3
60°
90°
110°
120°
146°
150°
180°
θ
c(3)
h(6)
XENON
c(6)
h(6)
ARGON
c(3)
h(3)
c(6)

Fig. 1

Relative first-order, threebody interaction $\Delta E_1/E_1^{(o)}$, for triangles a = b = 1, c (units of nearest-neighbor distance) of argon and xenon atoms, as a function of the angle θ between the sides a and b. The symbols h and c denote the hcp- and fcc-lattice, respectively; the number of triangles at a specific angle θ is given in parantheses.

The curve for k [illegible] es in between those for argon and xenon, whereas the r [illegible] der effect for neon shows very nearly the same behavior as [illegible] ne other rare gas atoms for $\theta < 110^{\circ}$; for larger values of θ it stays much closer to the horizontal axis.

It is easy to show that a typical curve as given in Fig. 1 stabilizes the hexagonal close-packed configuration. To see this we have indicated in the figure the important values $\theta = 110^{\circ}$ and 146° (hcp) and $\theta = 120^{\circ}$ and 180° (fcc), supplied the corresponding points of the curve with indices $\underline{h}$ (hexagonal) and $\underline{c}$ (cubic) and written in parentheses the number of triangles occurring for that value of θ in the corresponding structure.

To make an accurate comparison between the two lattices, we have to compare the values of ΔE_1 for a fixed value of E_1 itself, for example, at 120°. This transformation will flatten the curve between 120° and 180°, leave the zero-value at 110° unchanged and lower the value somewhat for an equilateral triangle. This, however, does not change the argument in any appreciable way.

To a very good approximation, the curve for $\Delta E_1/E_1$ ($\theta = 120^{\circ}$) increases (slowly and) linearly with θ between 120° and 180°. Let us indicate its value at 146° by X, at 180° by $X + \alpha$. Then at 120° the value is very nearly $X - \alpha$. At 110° we have a contribution which we denote by Y, with $Y \approx 0$. The comparison yields :

$$[E_1(\mathrm{fcc}) - E_1(\mathrm{hcp})]/E_1 = 6(X - \alpha) + 3(X + \alpha) - (6X + 3Y) = 3[(X - \alpha) - Y] > 0.$$

Since E_1 is positive, this means that the fcc-lattice has a higher (less negative) energy than the hcp-configuration, so that the hexagonal close-packed lattice is stabilized by first-order threebody interactions. This difference is an order of magnitude larger than that in static lattice energy based on pair-potentials; it has, therefore, the desired magnitude, but the wrong sign.

The peculiar behaviour of the $\Delta E_1/E_1$-curve (Fig. 1) is to be borne in mind; it will be of particular importance for the second-order calculation which we discuss in the following communication. The first- and second-order effects will then be combined to determine the total effect of threebody interactions, in the first two orders of perturbation theory, on the stability of the fcc-configurations for solids of the heavy rare gas atoms.

REFERENCES

1) B. M. Axilrod and E. Teller, J. Chem. Phys. 11, 299 (1943)

2) M. Born c. s., Series of Papers in Proc. Phil. Soc. Cambridge (1940-42), "On the Stability of Crystal Lattices";

M. Born and K. Huang, Dynamical Theory of Crystal Lattices, (Oxford, 1954), Chap. III

3) B. M. Axilrod, J. Chem. Phys. 17, 1349 (1949); 19, 719 (1951)

4) J. A. Prins, J. M. Dumoré and Lie Tiam Tjoan, Physica 18, 307(1952)

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

6) T. Kihara, Revs. Modern Phys. 25, 831 (1953)

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

8) L. Jansen and J. M. Dawson, J. Chem. Phys. 23, 482 (1955)

9) J. Cuthbert and J. W. Linnett, Trans. Faraday Soc. 54, 617 (1958)

10) J. W. Linnett and A. J. Pöe, Trans. Faraday Soc. 47, 1033 (1951)

11) H. Margenau, Revs Modern Phys. 11, 1 (1939)

12) B. M. Axilrod, J. Chem. Phys. 17, 1349 (1949); 19, 719, 724 (1951)

13) P. Rosen, J. Chem. Phys. 21, 1007 (1953)

14) A. Shostak, J. Chem. Phys. 23, 1808 (1955); see also P. O. Löwdin, ibid, 19, 1570, 1579, (1951) (ionic crystals)

15) R. U. Ayres and R. H. Tredgold, Phys. Rev. 100, 1257 (1955); Bull. Am. Phys. Soc. 1, 292 (1956)

16) T. Kihara, J. Phys. Soc. Japan 15, 1920 (1960)

17) Y. Muto, Proc. Phys.-Math. Soc. Japan 17, 629 (1943)

18) Y. Midzuno and T. Kihara, J. Phys. Soc. Japan 11, 1045 (1956)

19) W. L. Bade, J. Chem. Phys. 27, 1280 (1957)

20) W. L. Bade and J. G. Kirkwood, J. Chem. Phys. 27, 1084 (1957)

21) M. J. Sparnaay, Physica 25, 217 (1959)

22) R. T. McGinnies and L. Jansen, Phys. Rev. 101, 1301 (1956)

23) L. Jansen and R. T. McGinnies, Phys. Rev. 104, 961 (1956);
R. T. McGinnies, Ph. D. thesis, University of Maryland
(1957) (unpublished)

24) F. C. Brooks, Phys. Rev. 86, 92 (1952)

25) A. Dalgarno and J. T. Lewis, Proc. Roy. Soc. (London) A69, 57 (1956)

26) L. Jansen, Physica 23, 599 (1957); Phys. Rev. 110, 661 (1958)

27) L. Jansen, Phys. Rev. 125, 1798 (1962).

Geneva, January 31, 1963
LJ/if 190-18

ABSOLUTE STABILITY OF CUBIC CRYSTAL STRUCTURES OF HEAVY RARE GAS ATOMS II*.

Laurens Jansen and Samson Zimering.

Battelle Memorial Institute, International Division,
Geneva, Switzerland.

(Received)

There is a good experimental evidence that neon, argon, krypton and xenon crystallize in a face-centered cubic (fcc)-lattice, whereas helium, under pressure, forms crystals of hexagonal closest packing (hcp). This preference of heavy rare gas solids for the cubic configuration has been the subject of many investigations, but a satisfactory solution has so far not been found.

In a previous communication$^{1)}$ this problem has been outlined. It was supposed that short-range manybody interactions in these solids are significant and that the difference between these effects in the two close-packed structures (fcc and hcp) may be sufficiently large to overcome the small difference in static lattice energy based on pair-potentials, which favors the hcp-lattice.

---

* This research has been made possible through the support and sponsorship of the U. S. Department of Army, through its European Research Office.

First-order perturbation results, obtained on the basis of a Gaussian effective-electron model, for threebody interactions were seen to be unambiguously in favor of the hcp-structure. The triangles considered are formed by a central atom and any two of its twelve nearest neighbors in the two lattices. The remaining task is to calculate the second-order threebody interactions between heavy rare gas atoms, and then to combine the first- and second-order effects to provide a definite answer to the stability problem. Since rare gas crystals are held together by second-order (van der Waals) interactions, it is clear that a non-negligible threebody component in second order of perturbation theory may play a decisive role for the stability of such solids.

We will again make use of a Gaussian effective-electron model, i. e. one electron per atom with a charge distribution

$$\rho(r) = (\beta/\pi^{1/2})^3 \exp(-\beta^2 r^2) ; \tag{1}$$

β is a parameter characteristic for the rare gas atom considered.

Second-order interactions. Consider a triangle (abc) of atoms, and three effective electrons 1, 2, 3. We need not include spin variables in the wave function, so that we write in zero order (single Slater determinant)

$$\Psi_0 = [3!(1-\Delta^2_{abc})]^{-1/2} \det\{\varphi_a(1)\varphi_b(2)\varphi_c(3)\}, \ldots \tag{2}$$

where the overlap integral Δ_{abc} is given by

$$\Delta^2_{abc} = \Delta^2_{ab} + \Delta^2_{ac} + \Delta^2_{bc} - 2\Delta_{ab}\Delta_{ac}\Delta_{bc} ,$$

in terms of overlap integrals between pairs of atoms.

For the second-order energy we have to evaluate

$$E_2 = \sum_{\varkappa \neq o} \frac{(H'_{abc})_{o\varkappa}(H'_{abc})_{\varkappa o}}{E_o - E_\varkappa} \equiv - \frac{1}{E_{A\nu}} \langle \{H'_{abc} - \langle H'_{abc} \rangle\}^2 \rangle, \ldots \quad (3)$$

where $E_{A\nu}$ is an "average excitation energy" determined by the averaging procedure, H'_{abc} is the perturbation Hamiltonian for the system of three Gaussian atoms, $\varkappa$ numbers the excited states of the system (energy $E_\varkappa$), and where E_o is the unperturbed ground state energy. The brackets indicate an expectation value for the unperturbed ground state.

Since H'_{abc} can be taken directly from the first-order calculations 1)2), the only unknown quantity is $\langle H'_{abc}{}^2 \rangle$. We denote the sum of second-order energies between the three isolated pairs of atoms by $E_2^{(o)}$, so that

$$E_2^{(o)} = E_2^{(o)}{}_{(ab)} + E_2^{(o)}{}_{(ac)} + E_2^{(o)}{}_{(bc)},$$

and form the difference between E_2 and $E_2^{(o)}$,

$$\Delta E_2 = E_2 - E_2^{(o)} .$$

This difference gives the threebody component of E_2, which we will evaluate in relative magnitude

$$\Delta E_2 / E_2^{(o)} = (E_2 - E_2^{(o)})/E_2^{(o)} . \quad (4)$$

The expression for $E_2^{(o)}{}_{(ab)}$ is similar to that for E_2, with H'_{abc} replaced by H'_{ab}. It should be noted that the average excitation energies $E_{A\nu}$ occurring in the expression for E_2 and $E_2^{(o)}{}_{(ab)}$ are not necessarily the same quantity. Their difference can, however, be ignored for the present purposes[3)]. In forming, then, the ratio $\Delta E_2/E_2^{(o)}$ the quantities $E_{A\nu}$ cancel to a sufficient degree of accuracy.

The next step consists in substituting the explicit expression for the perturbation Hamilton H'_{abc}, which, of course, is simply the sum of the three pair-contributions, i. e.

$$H'_{abc} = H'_{ab} + H'_{ac} + H'_{bc} ,$$

together with the determinantal form for Ψ_o into eq. (4), and evaluating the various expectation values which occur. It is essential to avoid the use of multipole expansions; therefore we retain H'_{abc} in its exact form.

The resulting equation for $E_2^{(o)}$ is relatively simple. Let us introduce the notation

$$D_{ab} \equiv \iint \varphi_a^2\,(1)\,\varphi_b^2\,(2)\;H'^2_{ab}\;d\tau_1\,d\tau_2$$

and (5)

$$E_{ab} \equiv \iint \varphi_a\,(1)\;\varphi_b\,(1)\;\varphi_a\,(2)\;\varphi_b\,(2)\,H'^2_{ab}\;d\tau_1\;d\tau_2$$

for direct and exchange two-center integrals, respectively, with similar expressions for D_{ac}, E_{ac} and D_{bc}, E_{bc}. We find easily

$$- E_{Av} E_2^{(o)}(a\,b) = \frac{D_{ab} - E_{ab} \Delta_{ab}^2}{1 - \Delta_{ab}^2} - \langle H'_{ab} \rangle^2 \;;\; \text{etc.},$$

so that

$$- E_{Av} E_2^{(o)} = \frac{D_{ab} - E_{ab} \Delta_{ab}^2}{1 - \Delta_{ab}^2} + \frac{D_{ac} - E_{ac} \Delta_{ac}^2}{1 - \Delta_{ac}^2} + \frac{D_{bc} - E_{bc} \Delta_{bc}^2}{1 - \Delta_{bc}^2} -$$

$$- \left\{ \langle H'_{ab} \rangle^2 + \langle H'_{ac} \rangle^2 + \langle H'_{bc} \rangle^2 \right\} . \qquad (6)$$

On the other hand, the formal expression for $\langle H'^2_{abc} \rangle$ is already of considerable complexity. The square of Ψ_o contains 36 contributions, which leads, combined with H'^2_{abc}, to 21 different integrals. If we now decompose H'^2_{abc} into squares and double products,

$$H'^2_{abc} = H'^2_{ab} + H'^2_{ac} + H'^2_{bc} + 2H'_{ab}H'_{ac} + 2H'_{ab}H'_{bc} + 2H'_{ac}H'_{bc},$$

then there are in total 126 integrals to be evaluated, many of three-center type.

Fortunately, it appears that all these contributions to the second-order energy, and also the expression for $E_{A\nu}E_2^{(o)}$ (eq. 6), can be written as linear combinations of the following five basic integrals

$$A(x) = \frac{2}{x} e^{-x^2} \int_0^x e^{t^2}\, dt,$$

$$B(x) = \frac{\text{erf}\,.\,x}{x} \quad .$$

$$(7)$$

$$C(x) = \frac{e^{-x^2}}{x} \int_0^x e^{u^2} \left(\text{erf}.\,\frac{u}{\sqrt{2}}\right)^2 du$$

$$F(x) = \frac{2}{\sqrt{\pi}\cdot x} \int_0^\infty \left\{ e^{-[u^2 + (u-x)^2]} - e^{-[u^2 + (u+x)^2]} \int_0^x e^{t^2}\, dt \right\} du,$$

where x is a side of the triangle (abc), and

$$I\,(u,\ v,\ \theta) = \int_0^\infty \int_0^{2\pi} \int_0^{\pi} \{ (u^2 + x^2 - 2ux \sin\alpha \sin\beta)^{-1/2}\, [v^2 + x^2 - 2vx \sin\alpha \sin(\beta+\theta)]^{-1/2}.$$

$$\cdot \operatorname{erf}\left[(u^2 + x^2 - 2ux \sin\alpha \sin\beta)^{1/2}\right] \operatorname{erf}\left[(v^2 + x^2 - 2vx\sin\alpha \sin(\beta+\theta))^{1/2}\right] \cdot$$

$$\cdot\, x^2 e^{-x^2} \sin\alpha \Big\} \, d\alpha \, d\beta \, dx \,, \tag{7}$$

where u and v are two sides of the triangle and θ the angle between them.

In principle, the basic integrals (7) must be evaluated by electronic computation. It is fortunate, and rather surprising, to discover that asymptotic series expansions for these functions can be given with excellent precision. The precision is of the order of 10^{-6} for small values of the variables; this corresponds to the case of an equilateral triangle of the heaviest rare gas atoms. The precision is 10^{-12} for larger values of the variables (triangles with larger opening, and lighter atoms). An accuracy of 10^{-6} is sufficient for the present problem.

The asymptotic development makes it possible to evaluate the final result in analytic form; the expression is of the type of a sum of exponentially decreasing functions of the three sides of the triangle considered, plus a sum of inverse powers of these distances.

We consider here, as in the first-order calculations, triangles formed by a central atom and two of its twelve nearest neighbors; θ measures the angle formed by the two sides of the triangle originating at the central atom (see ref. 1 for details). Detailed results were obtained for an equilateral triangle, a 120°-configuration and a linear symmetric array of argon atoms; approximate values were already determined for the other important triangles $\theta = 110^{\circ}$ and $\theta = 146^{\circ}$ of the hcp-lattice. In addition, the behavior of $\Delta E_2/E_2^{(o)}$ as a function of θ for the other heavy rare gas atoms was established.

There appear to be two important contributions to the relative three-body component $\Delta E_2/E_2^{(o)}$:-

i) effects involving diatomic exchange only, i. e. terms arising from exchange of electrons between two of the three atoms on the triangle;

ii) effects due to triatomic exchange, i. e. those involving exchange of electrons between all three atoms on the triangle.

In the following Fig. 1 we plot these two components $\Delta E_2/E_2^{(o)}$ as a function of the angle θ, for a triplet of argon atoms. The resulting total effect is also given. (Fig. 1)

It is seen that the diatomic exchange effect starts from a rather high value at 60^o (0.28), decreases rapidly until $\theta \approx 110^o$, and then levels off very markedly (0.083 for $\theta = 120^o$ and 0.070 for $\theta = 180^o$), remaining positive. Since $E_2^{(o)}$ is negative, we see that diatomic exchange favors the formation of triangles with small opening. On the other hand, the triatomic exchange effect has opposite sign; it starts at a very high negative value (-0.49) at $\theta = 60^o$, decreases much more rapidly than the diatomic exchange until $\theta \approx 120^o$ (-0.028) and then remains almost constant (-0.01 at $\theta = 180^o$). Consequently, triatomic exchange favors triangles with large opening.

The total result for $\Delta E_2/E_2^{(o)}$, i. e. the sum of diatomic and triatomic exchanges, has a very surprising θ-dependence : the curve is practically identical with the one obtained in the first-order calculations (cf. Fig. 1 of ref. 1). The resulting value is approximately -0.20 at 60^o, increases rapidly until $\theta \approx 120^o$ and remains nearly the same for higher values of θ. At $\theta = 110^o$ the total value is close to zero. From the analytic form of the final result we conclude further that $\Delta E_2/E_2^{(o)}$ for neon, krypton and xenon behave in the same way as for the first-order effect.

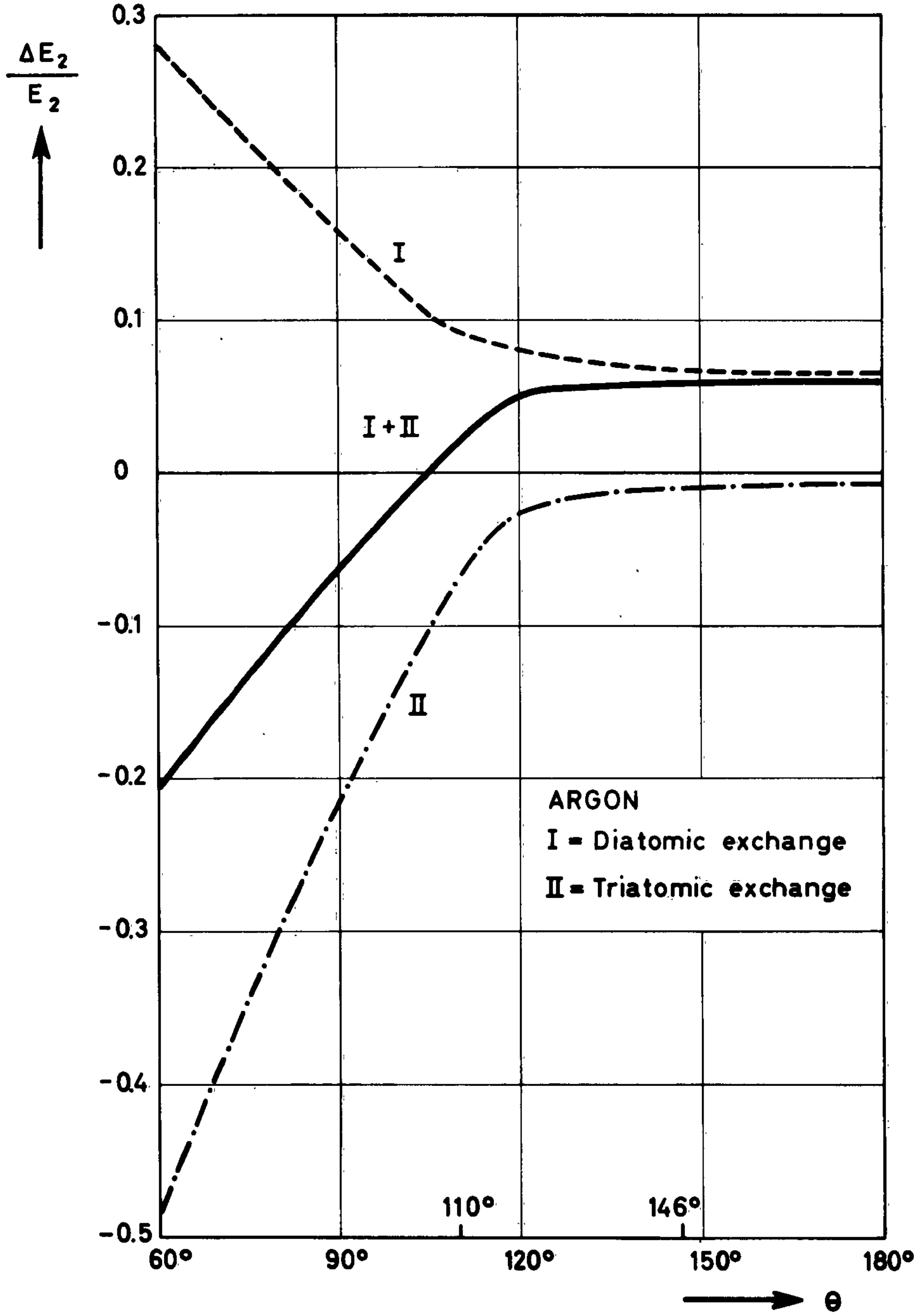

ΔE₂/E₂
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
I
I + II
II
ARGON
I = Diatomic exchange
II = Triatomic exchange
110°
146°
60°
90°
120°
150°
180°
θ

Fig. 1

Relative second-order, threebody interaction $\Delta E_2/E_2^{(o)}$, for triangles $a = b = 1$, c (units of nearest neighbor distance) as a function of the angle θ between the sides a and b. The curves I and II denote diatomic and triatomic exchange contributions, respectively; (I + II) is the total second-order effect.

We have now, in first- and second-orders of perturbation theory, two families of characteristic curves for the relative threebody interactions between atoms of the heavy rare gases which are very close indeed. Since these curves are all of the same type, the precise values of the dimensionless parameter βR (R is the nearest neighbor distance in the lattice) do not matter. The following stability considerations apply for neon, argon, krypton and xenon as well.

Let us consider the resulting second-order curve for argon. It was shown in ref. 1 that a curve of this type favors the hcp-structure in first order. Since, however, we now have that the second-order energy $E_2^{(o)}$ is negative, the same curve stabilizes the fcc-lattice in second order. Since the lattice energy is negative, the second-order effect will be more important than that of first order, so that the face-centered cubic structure is the more stable one for crystals of the heavy rare gas atoms.

To calculate this net-effect more precisely, we determine the ratio

$$\frac{\Delta E_1 + \Delta E_2}{E_1^{(o)} + E_2^{(o)}} \, .$$

Consider first an equilateral triangle of (argon) atoms, placed at nearest-neighbor distances from each other. In this configuration we have $E_2^{(o)} \approx - 2E_1^{(o)}$. Further, since we found that the first- and second-order relative effects are very nearly the same, we put $\Delta E_1/E_1^{(o)} = \Delta E_2/E_2^{(o)}$. The above ratio becomes now

$$\frac{\Delta E_1 + \Delta E_2}{E_1^{(o)} + E_2^{(o)}} \approx \frac{-\Delta E_1}{E_1^{(o)}} + 2\frac{\Delta E_2}{E_2^{(o)}} \doteq \frac{\Delta E_2}{E_2^{(o)}} \, .$$

so that the total relative threebody effect is given directly by the second-order contribution. For values of θ different from 60^o the ratio $-E_2^{(o)}/E_1^{(o)}$ for the triangles considered becomes larger than 2. This change is, however, very slow so that no appreciable error is involved in assuming a value 2 for all these configurations. Further we find that $\Delta E_2 \approx -2 \Delta E_1$, the same relation as there exists between $E_2^{(o)}$ and $E_1^{(o)}$.

We note also that the second-order effect agrees in sign with the Teller-Axilrod triple-dipole contribution4)5). Some of the general characteristics of this effect can, therefore, be taken over directly from the third-order triple-dipole interaction. The difference between the hcp- and fcc-structures is, however, at least an order of magnitude larger than the third-order effect. Further, whereas the triple-dipole effect averages out to zero at distances large compared to that between nearest neighbors because of its angular dependence, the present threebody interactions are of exchange type and, therefore, per se of short range.

In addition to explaining the stability of the face-centered cubic configuration for solids of the heavy rare gases the theory predicts, in particular, that the interaction between atoms in an equilateral triangular array will be 20 percent less negative than the sum of its pair-potentials. In this connection, a very recent investigation of the specific heat of solid argon (at constant volume) by Foreman and Lidiard6) is of great interest. For their calculation, these authors used the anharmonic Einstein model; from their results they estimated the free energy of formation of a vacancy. There is a discrepancy between these results and experimental values7)-9). Foreman and Lidiard suggest after careful analysis that the discrepancy can be due to the effect of threebody interactions and estimate a relative effect of about -25 % for an equilateral triangle of argon atoms. Our theoretical result is in agreement with their estimate.

The established stability of the cubic crystal structures for the heavy rare gas atoms is, so far, only valid at 0^{o}K. At non-zero temperatures the free energy determines stability. However, Barron and Domb 10) found that with increasing temperature the tendency shifts towards the cubic lattice for pair-potentials, although a transition from hexagonal to cubic occurs only in the neighborhood of the melting points of the solids. Since the threebody component is of short range, with a relatively large difference between the two lattices, a shift towards the hexagonal lattice at such low temperature is unlikely.

It may possibly also be anticipated that the unexplained difference in crystal structures occurring among the alkalihalides (for example NaCl and KCl on one hand, CsCl on the other hand) will find a similar explanation. We note that the corresponding ions are isoelectronic with the rare gas atoms. Preliminary investigations are in progress on this subject.

We emphasize again that the efficiency of the Gaussian model in this particular case may be mainly due to the fact that we are looking for the explanation of a phenomenon common to a number of different solids. As a consequence, we can base the calculations on a model which is more primitive than that required for a specific property of a specific atomic species.

Detailed results on all different triangular configurations will be published elsewhere. Finally, we wish to thank Mr R. Lenoir and his associates of the Computing Section for their assistance with the numerical calculations.

Genève, le 30.1.1963
LJ/SZ/if 190-18

REFERENCES

1) L. Jansen, Physics Letters ....

2) L. Jansen, Phys. Rev. 125, 1798 (1962)

3) L. Jansen and R. T. McGinnies, Phys. Rev. 104, 961 (1956)

4) B. M. Axilrod and E. Teller, J. Chem. Phys. 11, 299 (1943)

5) B. M. Axilrod, J. Chem. Phys. 17, 1349 (1949); 19, 719, 724 (1951)

6) A. J. E. Foreman and A. B. Lidiard, Phil. Mag. (in the press).
We thank these authors for sending us a preprint of their publication.

7) P. Flubacher, A. J. Leadbetter and J. A. Morrison, Proc. Phys. Soc. 78, 1449 (1961)

8) R. H. Beaumont, H. Chihara and J. A. Morrison, Proc. Phys. Soc. 78, 1482 (1961)

9) E. R. Dobbs and G. P. Jones, Reports on Progr. in Phys. 20, 516 (1957)

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

IMPLICATION OF RESULTS FOR POSSIBLE FUTURE WORK

With the completion of the analysis concerning the stability problem of heavy rare gas solids, one of the principal aims of the research project has been achieved. We hope that these results may be classified as a breakthrough in solid-state theory, since they concern the first absolute stability proof for any crystal structure occurring in nature.

In our opinion, we are also approaching the final solution to a different major problem in crystal physics : the explanation for the crystal structures of the heavy alkali halides (e. g., CsCl compared with NaCl and KCl) and the transitions (induced by pressure or temperature) occurring between these two crystal forms. There is an apparent close connection between the alkali halides and the heavy rare gas atoms : the ions of the alkali halides are isoelectronic with the rare gas atoms (Na^+, F^- with Ne; K^+, Cl^- with A; Rb^+, Br^- with Kr; Cs^+, I^- with Xe). It has been found in the literature that the Madelung energy, plus pair-potentials (van der Waals interactions), favors the NaCl-configuration by as much as one percent and the conclusion has been that the CsCl-structure should not occur at all (Cf. M. Born and K. Huang, "Dynamical Theory of Crystal Lattices" (Oxford, (1954), Chap. III). Since in this case the difference in pair-energy is so large, we understand already why the transition from one structure to the other with the alkali halides occurs only at the end of the isoelectronic series.

Now that direct experimental evidence for manybody interactions in rare gas solids also appears to have been established from the free energy of vacancy formation, we can envisage that the elastic constants, for example, of these solids will be measured in the near future. The theoretical analysis of the deviations from the Cauchy-relations, envisaged in original project, falls precisely in line with these recent developments.

It is interesting to observe that the occurrence of manybody interactions in heavy rare gas solids may be seen as a direct parallel to the recently discovered chemical reactivity of xenon. In our opinion, very significant results will be obtained in the near future on different phases of chemistry and solid-state properties of closed-shell atoms and molecules.

The interest of band theoretical calculations for such solids, in conjunction with an investigation of the relation between symmetry and band structure (and, consequently, electrical and optical properties), which we have already initiated, may increase considerably as a result of these developments.

PUBLICATIONS AND CONFERENCES

The results of the first-order calculations on the stability problem was published in Phys. Rev. 125, 1798 (1962). Two manuscripts on the final results of the analysis will be submitted to Physics Letters (Amsterdam) before February 1 of this year.

Colloquium talks on this research were delivered by the principal investigator at the Aeronautical Research Laboratories, Wright-Patterson Air Force Base, Dayton, Ohio (December 5, 1962) and at the Winter Institute of Quantum Chemistry and Solid-State Physics, University of Florida, Gainesville, Florida (December, 1962).

PERSONNEL ON THE CONTRACT

The following persons were employed part-time under the contract during the past year :

1) Dr Laurens Jansen, principal investigator
2) Mr Samson Zimering, part-time associate, University of Geneva
3) Dr Michael H. Boon, theoretical physicist, Battelle Memorial Institute, Geneva
4) Mr Raymond Lenoir, Mr Henri Abeille, Mrs Jolan Targonski, scientific personnel, Computing Section, Battelle Memorial Institute, Geneva
5) Dr Erminio Lombardi, visiting scientist, Institute of Technology, Milano, Italy (independent sources).

Dr Barbara Kohin, visiting scientist, the Catholic University of America, Washington, D. C., has in the meantime returned to the United States.

No changes in research policies by the Contractor have occurred during the period December 1, 1961 - November 30, 1962.

SUMMARY OF NUMBERS OF MANHOURS ON CONTRACT

The total numbers of manhours on the contract for the individuals mentioned in the previous section are :

- Dr Laurens Jansen : 750 hrs
- Mr Samson Zimering : 1000 hrs
- Dr Michael H. Boon : 750 hrs
- Mr Raymond Lenoir : 250 hrs
- Mr Henri Abeille : 200 hrs
- Mrs Jolan Targonski : 600 hrs
- Dr Erminio Lombardi : (independent)

Not listed are hours expended for secretarial services, preparation and processing of Technical Reports and similar items.

No important property was acquired during the contract period at direct contract expense.

Geneva, January 31, 1963
LJ/if Z-9219-18