

Stability of Crystals of Rare-Gas Atoms and Alkali Halides in Terms of Three-Body Interactions. I. Rare-Gas Crystals*

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Several attempts have been undertaken in the literature to explain the observed stability of the face-centered-cubic (fcc) configuration for rare-gas crystals (except helium), which structure, according to calculations based on pair potentials, should be somewhat less stable than that of hexagonal closest packing (hcp). These attempts have failed or the results been found to be inconclusive. It is shown here how the fcc stability can be explained in terms of three-body exchange interactions between nearest neighbors in the crystals. On the basis of detailed results for neon atoms, the stability analysis may be based on an effective-electron model with Gaussian distribution of charge. No multipole expansions are invoked. The three-body interactions in first and second orders of perturbation theory follow simple symmetry principles, and their combined effect stabilizes the fcc over the hcp structure by a difference of up to four percent of the cohesive energy for the heavier atoms. Finally crystal stability is considered in its relation to total cohesive energy, and energy of vacancy formation, for the close-packed structures.

INTRODUCTION

ONE of the essential problems in solid-state physics and crystal chemistry concerns the explanation of the stability of observed crystal structures and, as the case may be, the interpretation of transitions between different structures exhibited by one and the same chemical compound at different external pressures or temperatures.

In the history of the stability problem two classes of solids, namely, those of the rare-gas atoms and of the alkali halides, have, due to their simplicity, received extensive interest in the literature. A forerunner was Zwicky,¹ who in 1923 carried out calculations on the breaking strength of sodium chloride. Hund² undertook the first stability calculation for ionic solids, whereas Lennard-Jones and Ingham³ compared, for atomic solids, the lattice energies of the face-centered cubic, body-centered cubic, and simple-cubic lattices. Later Goldschmidt⁴ established empirical rules for predicting the lattice types of ionic and other structures from a knowledge of ionic and atomic radii alone.

A series of important analyses concerning the stability of alkali-halide crystals followed, first by Mayer,⁵ then by May⁶ and Jacobs.⁷ From the work of Born and Mayer⁸ dates the well-known Born-Mayer potential for ionic interactions, consisting of an exponentially decreasing repulsion at short distances, a $1/R$ -electrostatic interaction between the net ionic charges, and supplemented by relatively weak van der Waals forces. Born⁹ and his collaborators investigated in

detail the mechanical stability of cubic and hexagonal lattices with central forces between the atoms (mechanical stability refers to the *static* lattice energy only). Similar considerations were given by Nabarro and Varley¹⁰ for hexagonal structures with an additional interaction energy depending only on the volume of the solid (like the Fermi energy of free electrons).

The result of these analyses was that the rare gases should all crystallize in a hexagonal close-packed (hcp) structure, which is favored over the face-centered-cubic (fcc) configuration by about one-hundredth of one percent of the cohesive energy. This difference is extremely small, but it is remarkably constant with respect to allowed changes in the potential function.¹¹⁻¹⁴ Further, it has been shown that neither zero-point energy,^{14,15} nor the possibility of thermal transitions¹⁴ can invalidate this conclusion.

However, it is known from experiments that solid neon, argon, krypton, and xenon have fcc structure and that only He⁴ exhibits a hcp phase. In attempting to explain this deviation between theory and experiment it should be remembered that the predicted difference in lattice energy between the two structures is very small. Therefore, any explanation which singles out the rare-gas crystals as a special case is subject to uncertainty. For this reason we will enlarge the basis for the analysis by including also the stability of alkali-halide crystals. In this way, no ambiguity concerning experimental verification can arise.

According to the Born-Mayer theory of ionic solids all alkali halides should crystallize in the so-called sodium chloride modification, consisting of two inter-

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¹ F. Zwicky, *Physik Z.* **24**, 131 (1923).

² F. Hund, *Z. Physik* **34**, 833 (1925).

³ J. E. Lennard-Jones and A. E. Ingham, *Proc. Roy. Soc. (London)* **A107**, 636 (1925).

⁴ V. M. Goldschmidt, *Fortschr. Mineral.* **15**, 73 (1931).

⁵ J. E. Mayer, *J. Chem. Phys.* **1**, 327 (1933).

⁶ A. May, *Phys. Rev.* **52**, 339 (1937); **54**, 629 (1938).

⁷ R. B. Jacobs, *Phys. Rev.* **54**, 468 (1938).

⁸ M. Born and J. E. Mayer, *Z. Physik* **75**, 1 (1932).

⁹ M. Born c. s., *Proc. Cambridge Phil. Soc.* **36**, 160, 173 (1940); **38**, 62, 82 (1942); **40**, 262 (1944).

¹⁰ F. R. N. Nabarro and J. H. O. Varley, *Proc. Cambridge Phil. Soc.* **48**, 316 (1952).

¹¹ J. A. Prins, J. M. Dumoré, and Lie Tiam Tjoan, *Physica* **18**, 307 (1952).

¹² T. Kihara and S. Koba, *J. Phys. Soc. Japan* **7**, 348 (1952).

¹³ T. Kihara, *Rev. Mod. Phys.* **25**, 831 (1953).

¹⁴ T. H. K. Barron and C. Domb, *Proc. Roy. Soc. (London)* **A227**, 447 (1955).

¹⁵ L. Jansen and J. M. Dawson, *J. Chem. Phys.* **23**, 482 (1955).

penetrating face-centered-cubic lattices. This structure is favored over the cesium chloride modification, where the interpenetrating lattices are simple-cubic, by a few percent of the lattice energy. Since the lattice energy amounts to 150–200 kcal/mole, the predicted difference between the two structures amounts to a few kcal/mole in favor of the sodium chloride modification.

It is known from experiments that all Li, Na, K, and Rb halides, plus CsF, crystallize in the NaCl structure. However, CsCl, CsBr, and CsI exhibit the CsCl structure, contradicting the Born-Mayer theory. In addition, it is found that all K and Rb halides, except KF, show pressure transitions to the CsCl structure. Such transitions are indeed predicted by the Born-Mayer theory, but the calculated transition pressures are considerably higher than the experimental ones. For example, the experimental transition pressure for RbCl is 4.900 atm, the calculated value ≈ 35.000 atm. It appears, therefore, that the Born-Mayer theory *overestimates* the stability of the sodium chloride modification for the K, Rb, and Cs halides, with the possible exception of KF. On the other hand, for some of the halides with the smallest cations Li and Na, and also for CsF, the Born-Mayer theory predicts transitions to the CsCl structure which have experimentally not been found. This indicates the tendency of the theory to *underestimate* the stability of the NaCl modification for halides with rather *different sizes* of cation and anion. For excellent reviews of the stability problem for alkali-halide crystals we refer to the treatise by Born and Huang¹⁶ and to a recent analysis by Tosi and Fumi.¹⁷

It is to be noted that, since the cohesive energy of rare-gas crystals is only of the order of a few kcal/mole, compared with 150–200 kcal/mole for the alkali-halide solids, the predicted energy difference between the two crystal structures at normal pressures is for the alkali halides of the order of 10^4 times that between the two *close-packed configurations for rare-gas crystals*.

We postulate that the failure of the theory to reproduce the correct experimental properties of rare-gas crystals and alkali-halide solids *has the same physical explanation*. This assumption is based on the observation that the alkali-halide ions are isoelectronic with the rare-gas atoms. Consequently, the interactions between ions, on one hand, and between rare-gas atoms, on the other hand, are formally identical if we subtract the purely Coulombic ion-ion interactions and disregard polarization effects in view of the high symmetry of the unstrained ionic crystals. This simplifies the analysis considerably, since the difference between solid helium and the other rare-gas crystals cannot then, as Cuthbert and Linnett¹⁸ have suggested, be

ascribed to a difference between the two- and eight-electron outer shells of the atoms.

The above assumption leads to the practically only explanation that the deviations from theory for the stability of rare-gas crystals and solid alkali halides must be due to *considerable many-body components of the static interactions between the atoms or ions*. It must be expected that the many-body interactions may be limited to those between triplets of atoms (ions), since otherwise a molecular description of these solids would completely break down.

The triplet interactions must be of considerable magnitude, since the two-body potential barrier to be overcome for alkali-halide crystals is of the order of a few kcal/mole. This indicates that they must be of *exchange* type and, therefore, of short range, so that we may restrict ourselves to triplets of atoms or ions of small dimensions in the crystal. The pair-potential barrier for rare-gas crystals is very much lower, but here the differences in triplet configurations between the two structures are also very much smaller, as we will see.

POSSIBLE MANY-BODY INTERACTIONS AS APPLIED TO CRYSTAL STABILITY

The first explicit calculation of three-body interactions between atoms was carried out by Axilrod and Teller¹⁹ (triple-dipole effect). It concerns a *third-order* perturbation calculation of induced-dipole interactions between three nonoverlapping atoms, i.e., a straightforward extension of London's $1/R^6$ van der Waals interactions from second order. Axilrod²⁰ applied this effect to rare-gas crystals and found that it does favor the fcc configuration, but that the difference with the hcp structure is too small to account for the absolute stability of the cubic lattice. In addition, the limitation to dipole interactions and the exclusion of overlap (exchange forces) invalidate an application to the immediate neighborhood of an atom in the crystal. On the other hand, the triple-dipole effect has been found to account for experimental third-virial coefficients of compressed argon,²¹ where its application is justified.

It was also known that *first-order* interactions (overlap or exchange forces) between closed electron shells are not additive²²; the first explicit calculation was undertaken by Löwdin²³ for ionic crystals, followed by Rosen²⁴ and Shostak²⁵ for three helium atoms. There

¹⁹ B. M. Axilrod and E. Teller, J. Chem. Phys. **11**, 299 (1943).

²⁰ B. M. Axilrod, J. Chem. Phys. **17**, 1349 (1949); **19**, 719, 724 (1951).

²¹ H. W. Graber and R. D. Present, Phys. Rev. Letters **9**, 247 (1962).

²² H. Margenau, Rev. Mod. Phys. **11**, 1 (1939).

²³ P. O. Löwdin, *A Theoretical Investigation into Some Properties of Ionic Crystals* (Almqvist and Wilksell, Uppsala, 1948).

²⁴ P. Rosen, J. Chem. Phys. **21**, 1007 (1953).

²⁵ A. Shostak, J. Chem. Phys. **23**, 1808 (1955).

¹⁶ M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Chaps. I and II.

¹⁷ M. P. Tosi and F. G. Fumi, Phys. Chem. Solids **23**, 359 (1962).

¹⁸ J. Cuthbert and J. W. Linnett, Trans. Faraday Soc. **54**, 617 (1958).

exists a remarkable similarity between the relative three-body interactions in the Axilrod-Teller (relative to additive second-order forces) and the Rosen-Shostak (relative to additive first-order forces) calculations in that both relative effects are *negative* for an equilateral triangle, and *positive* for a linear array of atoms. No direct attempts were made to apply these effects to crystal stability. In addition, solid helium is not of direct importance as it exhibits hcp structure.

A number of different-type many-body interactions have further been reported, partly based on electrostatic effects in which overlap of charge clouds is treated classically, or on the Drude model of harmonic oscillations for the atoms with dipole interactions.²⁶ Finally, it was shown by the author and McGinnies^{27,28} that also *second-order* (van der Waals) interactions cease to be additive if exchange effects are taken into account. A tendency towards stabilization of the fcc structure for rare-gas crystals was observed for dipole-dipole and dipole-quadrupole interactions. None of the above effects can, however, be used as a key to the explanation of the stability of rare-gas crystals for one or more of the following reasons: (a) They concern systems of little direct interest (helium); (b) overlap effects are neglected or treated classically; (c) the use of a multipole expansion for the interactions between the atoms.

On the other hand, it appears possible to base the analysis on a model which is sufficiently simple for numerical calculations, which avoids the defects mentioned above and which retains the possibly essential features of the stability problem.²⁶ We observe, first that preference for one or the other of the crystal structures under consideration is not an isolated property of a specific rare gas or alkali halide, but that it is *common* to a number of representatives from both series. Consequently, this preference cannot depend sensitively on the precise analytic form of the wave functions, but it must be determined by some general parameters characterizing the electron-charge distributions of the atoms or ions.

Further, explicit calculations with neon wave functions²⁸ have shown that (i) contributions to three-body interactions arising from exchange of more than one pair of electrons (multiple exchange) between the *same* pair of atoms are not important for densities up to that of the crystal; (ii) coupling of inter- and intra-atomic exchange effects may also be neglected. Since neon crystallizes already in the cubic configuration, it follows that also for the other rare-gas crystals we may neglect effects due to multiple and coupled exchange.

We are then left with an average of *single-exchange* effects, each term involving one electron of each atom (ion) of a pair. This average may be replaced by an exchange between "*effective*" electrons, one such electron

per atom (ion), each representing an average of the charge distribution of that atom (ion). The problem becomes then formally the same as that for three hydrogen atoms with parallel spins of the electrons.²⁹

The charge distribution of the effective electrons is chosen to be of Gaussian form

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

where r is the distance from the effective electron to its nucleus and where β is a parameter which can be determined empirically. Since crystal stability depends critically on the interactions between atoms (or ions), we choose β such that it fits the $1/R^6$ part of an empirical potential function, which yields values of β between 1.07 and 0.454 in units of 10^8 cm^{-1} from neon to xenon.²⁸ A sensitive test is then to see how well these values of β agree with the repulsive (first-order) part of an interatomic potential function. The agreement is excellent for neon, whereas for the heavier rare-gas atoms β appears to increase somewhat with decreasing interatomic distances.²⁶ It should be noted that the precise values of β do not matter for stability, since we are only interested in a *range* of such values for the heavy rare-gas atoms. For alkali-halide ions it is generally necessary to use different β values for cation and anion of the same halide. We will return to this problem in a following publication.

After this simplification of the stability problem, first- and second-order perturbation calculations are carried out for triplets of atoms (ions), and the result is summed over the lattices. Since the three-body interactions are of exchange type and, therefore, of very short range, we will limit ourselves to triplets formed by a central atom and any two of its *nearest* neighbors. In the case of alkali halides it proves generally necessary to include also triplets formed by a central ion and any two of its *next nearest* neighbors.

RARE-GAS ATOMS: FIRST- AND SECOND-ORDER THREE-BODY EXCHANGE INTERACTIONS

We will now evaluate first- and second-order interactions for a triplet (abc) of rare-gas atoms; the electron charge distribution of each atom is replaced by that of an effective electron with characteristic parameter β as given by Eq. (1). For the atomic wave functions we take

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

the zero-order wave function for the triplet is then (Slater determinant)

$$\Psi = [3!(1 - \Delta_{abc}^2)]^{-1/2} \det\{\varphi_a(1)\varphi_b(2)\varphi_c(3)\}, \quad (3)$$

²⁶ cf. L. Jansen, Phys. Rev. **125**, 1798 (1962) for detailed references.

²⁷ R. T. McGinnies and L. Jansen, Phys. Rev. **101**, 1301 (1956).

²⁸ L. Jansen and R. T. McGinnies, Phys. Rev. **104**, 961 (1956).

²⁹ To represent also ions with charges plus one and minus one, we should formally use two effective electrons per ion, counterbalanced by nuclear charges of plus three and plus one, respectively. The exchange effect then becomes formally the same as that between ions of lithium hydride. However, we will subtract electrostatic interactions between the net charges from the outset, so that ions and atoms can be represented by the same model.

where a, b, c denote the atoms, 1, 2, 3, the effective electrons, and where

$$\Delta_{abc}^2 = \Delta_{ab}^2 + \Delta_{ac}^2 + \Delta_{bc}^2 - 2\Delta_{ab}\Delta_{ac}\Delta_{bc} \quad (4)$$

in terms of the overlap integrals Δ_{ab} , etc., between the different pairs of atoms. The perturbation Hamiltonian, H_{abc}' , can be written as

$$H_{abc}' = H_{ab}' + H_{ac}' + H_{bc}' ,$$

in terms of the perturbations between the different pairs. An essential advantage of the Gaussian effective-electron model is that it enables us to evaluate all three-center integrals numerically *without* making use of multipole expansions. This is important, since it is known³⁰⁻³² that first- and second-order multipole series are only semiconvergent (asymptotic series).

First-Order Calculations

The results of the first-order perturbation calculation for triplets of rare-gas atoms have been given earlier.^{26,33} Let $E_1 = \langle H_{abc}' \rangle$ denote the *total* first-order energy for the triplet (abc) , where the expectation value is determined with the zero-order wave function (3), and let $E_1^{(0)} = \langle H_{abc}' \rangle^{(0)}$ denote the sum of first-order interactions between the three *isolated pairs* of atoms which form the triangle, with the corresponding zero-order pair wave functions. We determine the relative three-body component of the first-order energy, i.e.,

$$\Delta E_1/E_1^{(0)} \equiv (E_1 - E_1^{(0)})/E_1^{(0)} , \quad (5)$$

as a function of β and of the triangular dimensions. For the application to the stability problem of rare-gas crystals we limit ourselves, as stated before, to triangles formed by a central atom and any two of its nearest neighbors in the crystal. There are 12 nearest neighbors in both the fcc and the hcp structures, so that we have 66 of such triangles in either lattice. Any one of these isosceles triangles is specified by the nearest-neighbor distance, R , in the crystal and by the opening, θ , of the triangle at the central atom. It appears that $\Delta E_1/E_1^{(0)}$ is only a function of the dimensionless parameter βR , and of θ .

All first-order integrals occurring³⁴ in E_1 and $E_1^{(0)}$ can be written as products of overlap integrals (Δ_{ab} , Δ_{ac} , etc.) and the function

$$F(x^2) \equiv \frac{1}{x} \int_0^x \exp(-y^2) dy = (\pi^{1/2}/2) \frac{\operatorname{erf} x}{x}$$

for different values of x . They can readily be evaluated, since, e.g.,

$$\Delta_{ab}^2 = \exp(-\beta^2 R_{ab}^2/2) ,$$

³⁰ F. C. Brooks, Phys. Rev. **86**, 92 (1952).

³¹ A. Dalgarno and F. T. Lewis, Proc. Roy. Soc. (London) **A69**, 57 (1956).

³² L. Jansen, Physica **23**, 599 (1957); Phys. Rev. **110**, 661 (1958).

³³ L. Jansen, Phys. Letters **4**, 91 (1963).

³⁴ A list of these integrals is given in Table II of Ref. 26.

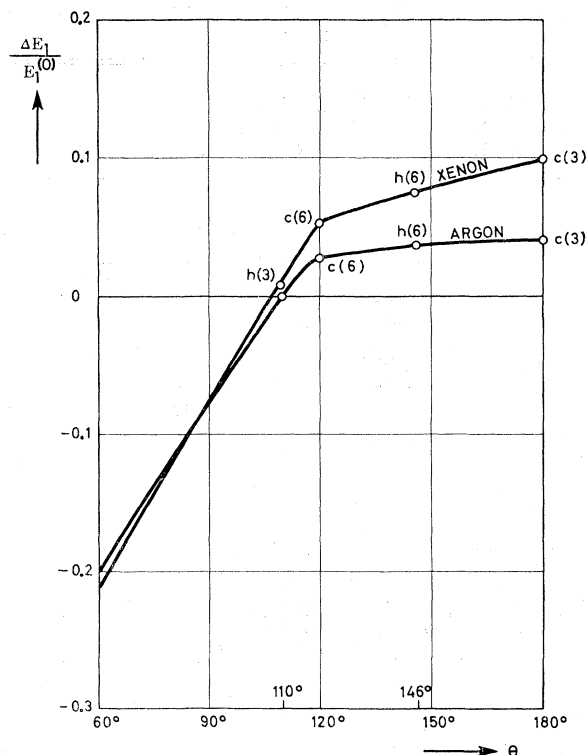


FIG. 1. Relative first-order, three-body interaction $\Delta E_1/E_1^{(0)}$, for triangles $a=b=1, c$ (units of nearest-neighbor distance) of argon and xenon atoms, as a function of the angle θ between the sides a and b . The symbols h and c denote the hcp and fcc lattice, respectively; the number of triangles at a specific angle θ is given in parentheses.

for Gaussian distributions (R_{ab} is the internuclear distance between atoms a and b), and $F(x^2)$ may be determined by interpolation, using *Tables of the Error Function and its Derivative* (Natl. Bureau of Standards, Washington, 1935). For solid neon, argon, krypton, and xenon the values of βR are 3.44, 2.40, 2.10, and 1.99, respectively. The results for $\Delta E_1/E_1^{(0)}$ for solid argon and xenon are given in Fig. 1 and in Table II of Appendix III, as a function of the opening θ of the triangle at the central atom.

The values for solid krypton lie in between those for argon and xenon; for solid neon the results are not sufficiently accurate because all three-body interactions become very small; they indicate that the negative part of $\Delta E_1/E_1^{(0)}$ is close to those of argon and xenon, but that the positive part ($\theta > 110^\circ$) lies close to the horizontal axis.

We note that for values of θ between 60° and 110° , $\Delta E_1/E_1^{(0)}$ is negative, implying that three-body interactions of such triangles *decrease the interatomic repulsion*; for θ larger than 110° the first-order interactions are *more repulsive* than the sum of interactions for the three isolated pairs. This change of sign agrees with the results found by Rosen²⁴ (Shostak²⁵ analyzed only the case $\theta = 180^\circ$ for three helium atoms).

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.
hcp	1, 1, 8/3	110°	3	1, 1, 11/3	146°	6
fcc	1, 1, 3	120°	6	1, 1, 4	180°	3

It is easy to show that a curve of the type as given in Fig. 1 stabilizes the hexagonal close-packed configuration. To see this we determine first the differences in triangular arrangements between the fcc and hcp structures, i.e., we compare the 66 triangles formed by a central atom and any two of its 12 nearest neighbors in the two lattices. It appears that of these 66 triangles 57 are the same between the two structures, but 9 are different. The dimensions of these 9 triangles and the corresponding values of θ are given in Table I (a, b, c , stand here not for the atoms, but for the sides of the triangle in units of nearest-neighbor distance).

For a comparison with $\Delta E_1/E_1^{(0)}$ we have, in Fig. 1, also indicated the important values $\theta=110^\circ$ and 146° (hcp) and $\theta=120^\circ$ and 180° (fcc), supplied the corresponding points of the curves with h (hexagonal) and c (cubic) and written in parentheses the number of triangles for that value of θ in the corresponding structure, according to Table I.

Since the coordination number of the two structures is the same, we determine the first-order energies for the same values of βR . To compare the two lattices the values of ΔE_1 have to be calculated for a fixed value of $E_1^{(0)}$ itself, for example, at $\theta=120^\circ$. This transformation of the total pair interactions may be carried out according to a $1/R^{12}$ dependence, or an exponential decrease of the pair repulsion, which makes very little difference. It flattens the curve for $\Delta E_1/E_1^{(0)}$ slightly between $\theta=120^\circ$ and 180° , leaves the zero value at $\theta \approx 110^\circ$ unchanged and lowers the value for an equilateral triangle somewhat. This, however, does not affect the following argument.

In good approximation $\Delta E_1/E_1^{(0)}$ 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 $X-\alpha$, whereas at $\theta=110^\circ$ the contribution is $Y \approx 0$. The comparison yields ($E_1^{(0)}$ evaluated at fixed θ):

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

Since $E_1^{(0)}$ is always positive, this means that the fcc lattice has a higher (positive) first-order energy than the hcp configuration, so that the hexagonal close-packed lattice is stabilized by first-order three-body interactions. Numerically, this difference is found to be a few percent of the first-order lattice energy; it is, therefore, of the correct order of magnitude, but has the wrong sign. The type of curve of Fig. 1 is of particular importance also for second-order three-body interactions.

Second-Order Calculations

Since rare-gas crystals are held together by second-order (van der Waals) interactions, three-body components of such forces may be of essential importance for crystal stability. This expectation is confirmed by the results of the following analysis, of which preliminary results have been published elsewhere.^{35,36}

We consider again a triangle (abc) of atoms and three effective electrons 1, 2, 3. For the second-order energy one has to evaluate

$$E_2 = \sum_{\kappa \neq 0} \frac{(H_{abc'})_{0\kappa} (H_{abc'})_{\kappa 0}}{E_0 - E_\kappa} \equiv -\frac{1}{E_{av}} \langle [H_{abc'} - \langle H_{abc'} \rangle]^2 \rangle, \quad (7)$$

where E_{av} is an average excitation energy defined by the averaging procedure. The index κ numbers the excited states of the system (energy E_κ), E_0 is the unperturbed ground-state energy. The brackets denote again an expectation value for the ground-state wave function (3).

Since $\langle H_{abc'} \rangle$ can be taken directly from the first-order calculations, the only unknown quantity is $\langle H_{abc'}^2 \rangle$. Let $E_2^{(0)}$ denote the sum of second-order energies between the three isolated pairs of atoms which form the triangle. Then the quantity

$$\Delta E_2/E_2^{(0)} = (E_2 - E_2^{(0)})/E_2^{(0)} \quad (8)$$

measures the relative second-order three-body interactions for the given triplet of atoms. It should be noted that the average excitation energies defined by the expressions for E_2 and $E_2^{(0)}$ are not necessarily the same quantities. It can be shown,²⁸ however, that their difference may be ignored for the present purposes. In forming, then, the ratio $\Delta E_2/E_2^{(0)}$, the quantities E_{av} cancel to a sufficient degree of accuracy.

The next step consists in substituting the explicit expression for $H_{abc'}$ in Eq. (7), together with the determinantal wave function (3), and in evaluating the various expectation values which occur. We retain again $H_{abc'}$ in its exact form, i.e., no multipole expansions are invoked for the interactions.

Whereas the resulting equation for $E_2^{(0)}$ is relatively simple, the formal expression for $\langle H_{abc'}^2 \rangle$ is already of considerable complexity. The square of Ψ contains 21 different terms and, if we decompose $H_{abc'}^2$ into squares and double products,

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

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

³⁵ L. Jansen, *Phil. Mag.* **8**, 1305 (1963).

³⁶ L. Jansen and S. Zimring, *Phys. Letters* **4**, 95 (1963).

To arrange these terms and simplify the notation, we follow a *two-step* procedure.³⁷ First, it appears possible to express $E_2^{(0)}$ and $\langle H_{abc} \rangle$ as a linear combination of eight *auxiliary functions* \mathcal{A} , \mathcal{B} , \mathcal{C} , \mathcal{D} , \mathcal{E} , \mathcal{F} , \mathcal{G} , and \mathcal{H} . It is then found that these auxiliary functions,

in turn, are all linear combinations of nine *basic integrals* K , L , M , N , O , P , Q , R and S . For the following we will use only dimensionless distances βR_{ab} , etc., where β is the Gaussian parameter.

The auxiliary functions are defined as follows:

$$\beta^2 \mathcal{A}(\beta R_{ab}) = \int \int \varphi_a^2(1) \varphi_b^2(2) H_{ab}{}^{\prime 2} d\tau_1 d\tau_2; \quad (9)$$

$$\beta^2 \Delta_{ab}{}^2 \mathcal{B}(\beta R_{ab}) = \int \int \varphi_a(1) \varphi_a(2) \varphi_b(1) \varphi_b(2) H_{ab}{}^{\prime 2} d\tau_1 d\tau_2; \quad (10)$$

$$\beta^2 \mathcal{C}(\beta R_{ab}, \beta R_{ac}, \angle bac) = \int \int \int \varphi_a^2(1) \varphi_b^2(2) \varphi_c^2(3) H_{ab}{}^{\prime} H_{ac}{}^{\prime} d\tau_1 d\tau_2 d\tau_3; \quad (11)$$

$$\beta^2 \Delta_{ab}{}^2 \mathcal{D}(\beta R_{ac}, \beta R_{c(ab)}, \angle ac(ab)) = \int \int \int \varphi_a(1) \varphi_a(2) \varphi_b(1) \varphi_b(2) \varphi_c^2(3) H_{ac}{}^{\prime 2} d\tau_1 d\tau_2 d\tau_3; \quad (12)$$

$$\beta^2 \Delta_{ab}{}^2 \mathcal{E}(\beta R_{ac}, \beta R_{bc}, \beta R_{c(ab)}) = \int \int \int \varphi_a(1) \varphi_a(2) \varphi_b(1) \varphi_b(2) \varphi_c^2(3) H_{ac}{}^{\prime} H_{bc}{}^{\prime} d\tau_1 d\tau_2 d\tau_3; \quad (13)$$

$$\beta^2 \Delta_{ab}{}^2 \mathcal{F}(\beta R_{ab}, \beta R_{ac}, \beta R_{c(ab)}) = \int \int \int \varphi_a(1) \varphi_a(2) \varphi_b(1) \varphi_b(2) \varphi_c^2(3) H_{ab}{}^{\prime} H_{ac}{}^{\prime} d\tau_1 d\tau_2 d\tau_3; \quad (14)$$

$$\beta^2 \Delta_{ab} \Delta_{ac} \Delta_{bc} \mathcal{G}(\beta R_{ab}, \beta R_{a(bc)}, \beta R_{(ab)(bc)}) = \int \int \int \varphi_a(1) \varphi_a(2) \varphi_b(2) \varphi_b(3) \varphi_c(1) \varphi_c(3) H_{ab}{}^{\prime 2} d\tau_1 d\tau_2 d\tau_3; \quad (15)$$

$$\beta^2 \Delta_{ab} \Delta_{ac} \Delta_{bc} \mathcal{H}(\beta R_{ac}, \beta R_{bc}, \beta R_{b(ac)}) = \int \int \int \varphi_a(1) \varphi_a(2) \varphi_b(2) \varphi_b(3) \varphi_c(1) \varphi_c(3) H_{ac}{}^{\prime} H_{bc}{}^{\prime} d\tau_1 d\tau_2 d\tau_3. \quad (16)$$

Similar expressions are obtained by permuting a , b , and c . In the above notation $R_{c(ab)}$ denotes the distance between atom c and the middle of R_{ab} , whereas $R_{(ab)(bc)}$ stands for the distance between the middles of R_{ab} and R_{bc} . Further, $\angle bac$ denotes the angle between R_{ab} and R_{ac} , $\angle ac(ab)$ the angle between R_{ac} and $R_{c(ab)}$, etc.

When we substitute the explicit expressions for $H_{ab}{}^{\prime}$, etc., into (9)–(16) then it appears upon inspection that the auxiliary functions are linear combinations of the following nine basic integrals:

$$K(x) = \frac{2}{x} \int_0^x e^{t^2} dt; \quad (17)$$

$$L(x) = \frac{\operatorname{erf} x}{x} = \frac{2}{x\pi^{1/2}} \int_0^x e^{-t^2} dt; \quad (18)$$

$$M(x) = \frac{e^{-x^2}}{x} \int_0^x e^{u^2} [\operatorname{erf}(u/2^{1/2})]^2 du; \quad (19)$$

$$N(x) = (2/x\pi^{1/2}) \int_0^\infty (e^{-[u^2+(u-x)^2]} - e^{-[u^2+(u+x)^2]}) \int_0^u e^{t^2} dt du; \quad (20)$$

$$O(u, v, \theta) = \int_0^\infty \int_0^{2\pi} \int_0^\pi x^2 e^{-x^2} (u^2 + x^2 - 2ux \sin \alpha \sin \gamma)^{-1/2} [v^2 + x^2 - 2vx \sin \alpha \sin(\gamma + \theta)]^{-1/2} \sin \alpha d\alpha d\gamma dx; \quad (21)$$

$$P(u, v, \theta) = \int_0^\infty \int_0^{2\pi} \int_0^\pi x^2 e^{-x^2} (u^2 + x^2 - 2ux \sin \alpha \sin \gamma)^{-1/2} [v^2 + x^2 - 2vx \sin \alpha \sin(\gamma + \theta)]^{-1/2} \times \operatorname{erf}[(v^2 + x^2 - 2vx \sin \alpha \sin \gamma)^{1/2}] \sin \alpha d\alpha d\gamma dx; \quad (22)$$

³⁷ The following mathematical analysis is essentially due to my collaborator, Samson Zimring.

$$Q(u, v, \theta) = \int_0^\infty \int_0^{2\pi} \int_0^\pi x^2 e^{-x^2} (u^2 + x^2 - 2ux \sin \alpha \sin \gamma)^{-1/2} [v^2 + x^2 - 2vx \sin \alpha \sin(\gamma + \theta)]^{-1/2} \\ \times \operatorname{erf}[(u^2 + x^2 - 2ux \sin \alpha \sin \gamma)^{1/2}] \operatorname{erf}[(v^2 + x^2 - 2vx \sin \alpha \sin(\gamma + \theta))^{1/2}] \sin \alpha d\alpha d\gamma dx; \quad (23)$$

$$R(x) = 1 - x^2 L^2(x) + (2/\pi^{1/2}) [L(x 2^{1/2}) - e^{-x^2} L(x)]; \quad (24)$$

$$S(x) = (4/x) \int_0^\infty [e^{-(u-x)^2} - e^{-(u+x)^2}] \left(\int_0^u e^{-t^2} dt \right)^2 du. \quad (25)$$

It is seen that the integrals O and P are special cases of the general integral Q , namely, those cases in which the first, then the second of the error functions occurring in the integrand of Q is replaced by 1, respectively. It is found also that the integral R is a special case of O and that S is a special case of Q , through the relations

$$R(x) = O(x, 0, 0^\circ) \quad \text{and} \quad S(x) = Q(x, x, 0^\circ). \quad (26)$$

The linear relations between the auxiliary functions \mathcal{A} to \mathcal{H} and the basic integrals K to S are given in Appendix I.

We can now write the second-order pair energy, $E_2^{(0)}$, for the triplet (abc) and the expectation value $\langle H_{abc}^{\prime 2} \rangle$ occurring in the total second-order energy E_2 [Eq. (6)] in terms of the auxiliary functions, as follows:

$$-E_{av} E_2^{(0)} / \beta^2 e^4 = \frac{\mathcal{A}(\beta R_{ab}) - \Delta_{ab}^2 \mathcal{B}(\beta R_{ab})}{1 - \Delta_{ab}^2} - \langle H_{ab}^{\prime 2} \rangle / \beta^2 e^4 + [(ac), (bc)], \quad (27)$$

where e is the electronic charge, and where $[(ac), (bc)]$ signifies that the corresponding expressions for the pairs ac and bc must be added. The expression for $\langle H_{abc}^{\prime 2} \rangle$ can be taken directly from the first-order calculations.

The equation for $\langle H_{abc}^{\prime 2} \rangle$ reads

$$(1 - \Delta_{abc}^2) \langle H_{abc}^{\prime 2} \rangle / \beta^2 e^4 = \{ \mathcal{A}(\beta R_{ab}) - \Delta_{ab}^2 \mathcal{B}(\beta R_{ab}) + 2\mathcal{C}(\beta R_{ab}, \beta R_{ac}, \beta R_{bc}) - 2\Delta_{ab}^2 \mathcal{D}(\beta R_{ac}, \beta R_{bc}, \beta R_{c(ab)}) \\ + [(ac), (bc)] \} + \{ -\Delta_{ab}^2 \mathcal{D}(\beta R_{ac}, \beta R_{c(ab)}, \beta R_{c(ab)}) - 2\Delta_{ab}^2 \mathcal{F}(\beta R_{ab}, \beta R_{ac}, \beta R_{c(ab)}) \\ + \Delta_{ab} \Delta_{ac} \Delta_{bc} \mathcal{G}(\beta R_{ab}, \beta R_{c(ab)}, \beta R_{c(ab)}) + 2\Delta_{ab} \Delta_{ac} \Delta_{bc} \mathcal{H}(\beta R_{ab}, \beta R_{ac}, \beta R_{c(ab)}) \\ + [(ba), (ac), (ca), (bc), (cb)] \}. \quad (28)$$

It is to be noted that the total number of permutations for the last four terms is six, compared with three for the first four terms of (28), since for the last terms permuting a and b , or a and c , or b and c is geometrically different for the arguments of the functions \mathcal{D} , \mathcal{F} , \mathcal{G} , and \mathcal{H} . In the first two terms on the right of (28) one recognizes again part of the two-body interaction for the pair ab , but the normalization constant has changed from $1 - \Delta_{ab}^2$ to $1 - \Delta_{abc}^2$. The difference between these terms of (28) and (27) leads then to three-body effects which are purely due to overlap.

The final step in the evaluation of the relative second-order three-body interactions involves substituting the corresponding linear combinations of the basic integrals (17)–(25) for the auxiliary functions in (27) and (28) and computing the basic integrals for the arguments determined by the triangles considered. In principle, the basic integrals must be evaluated by electronic computation. However, it was found that for many isosceles triangles, *asymptotic series expansions* which are sufficiently accurate can be given for these integrals. The two parameters which determine the accuracy of these series are βR (R is the length of the two equal sides of the triangle and β is the Gaussian parameter) and the opening, θ , of the triangle at the

central atom. For small βR , i.e., for the heavy rare-gas solids, and $\theta < 90^\circ$ the series have to be replaced by machine calculations. For all other configurations the final relative three-body interactions can be evaluated in analytic form; the expressions are of the type of a sum of exponentially decreasing functions of the triangular dimensions, plus a sum of inverse powers of these dimensions. We list in Appendix II the asymptotic series used; further details on the calculations and error estimates are given in a separate report.³⁸ Some numerical results for the auxiliary functions are compiled in Table IV of Appendix III.

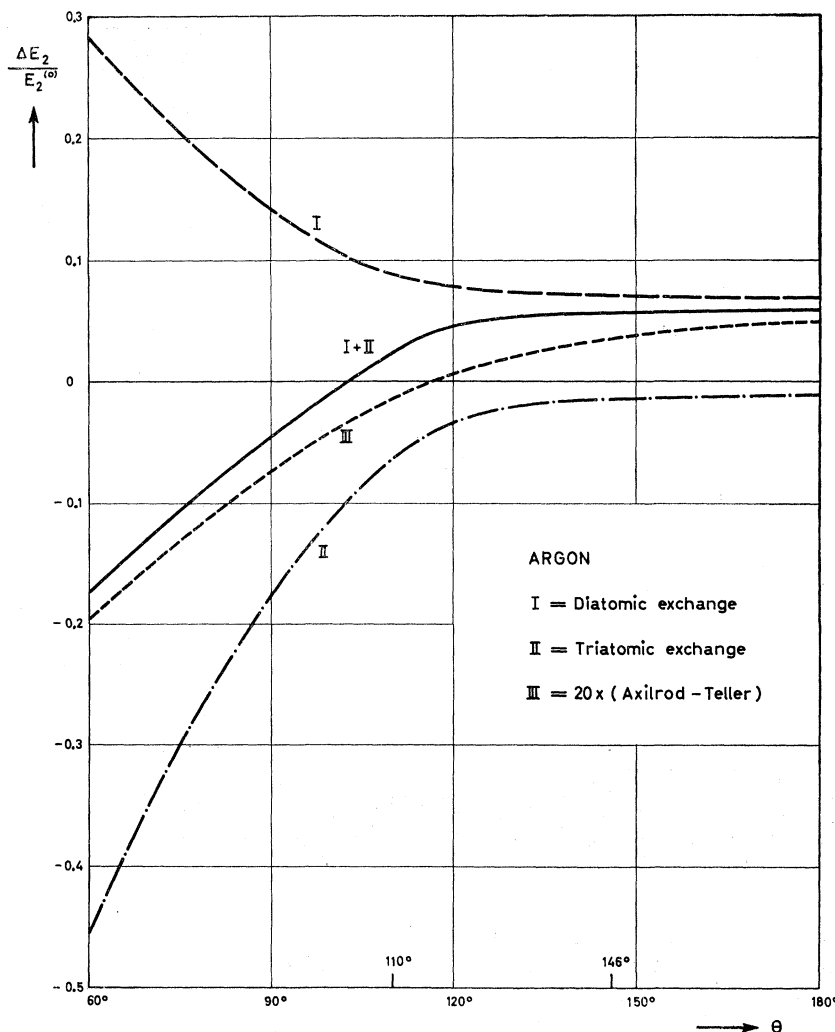
We consider, as in the first-order calculations, triangles formed by a central atom and two of its twelve nearest neighbors in the hcp and fcc configurations. The relative second-order three-body interactions (8) are functions only of βR and of θ .

In Fig. 2 and in Table III of Appendix III, $\Delta E_2/E_2^{(0)}$ is given as a function of θ for solid argon ($\beta R = 2.4$). There appear to be two important contributions to $\Delta E_2/E_2^{(0)}$, due to:

- (i) effects involving *diatomic exchange* only, i.e.,

³⁸ S. Zimering and L. Jansen, Technical Report 2846-6, BMI-Geneva, July 1963 (unpublished). Copies of this report are available upon request.

FIG. 2. Relative second-order, three-body interaction $\Delta E_2/E_2^{(0)}$, 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. Curve III represents the Axilrod-Teller (third-order) effect, magnified twenty times.



terms arising from exchange of electrons between two of the three atoms on the triangle (curve I);

(ii) effects of *triatomic exchange*, i.e., those involving all three atoms on the triangle (curve II).

The total result for $\Delta E_2/E_2^{(0)}$, i.e., the sum of diatomic and triatomic exchange effects (curve I+II) has a surprising θ dependence: *It is practically identical with the one obtained for the first-order effect.* From the analytical form of the final result we conclude further that $\Delta E_2/E_2^{(0)}$ for neon, krypton, and xenon behaves in the same way as the first-order effects for these solids.

Since the total pair energy, $E_2^{(0)}$, for the triangles is always negative, we conclude that for values of θ between 60° and approximately 110° three-body second-order interactions *decrease* the interatomic attraction compared with an additive sum-over-pairs; for larger values of θ the three-body forces are *attractive*. This change of sign agrees with the third-order Axilrod-Teller effect, which is also plotted in Fig. 2 (curve III).

It is observed that the second-order exchange forces are approximately *20 times larger* than the third-order three-body interactions, and that the exchange effect exhibits a much stronger θ dependence between $\theta=90^\circ$ and 120° .

The $\Delta E_1/E_1^{(0)}$ and $\Delta E_2/E_2^{(0)}$ curves are of the *same type*. Therefore, we can follow the same analysis as given in first order concerning stability. Since $E_1^{(0)}$ and $E_2^{(0)}$ have *opposite* sign, the conclusion is now reversed: *Second-order three-body interactions favor the face-centered-cubic configuration for rare-gas crystals.* Summed over the triangles listed in Table I this difference, relative to the total two-body energy of the crystals, is of the order of one percent in favor of the fcc structure for argon, krypton, and xenon [on the basis of Eq. (6)].

TOTAL THREE-BODY EXCHANGE INTERACTIONS AND CRYSTAL STABILITY

In Fig. 3 we compare the relative three-body interactions in first- and second-order for isosceles triangles

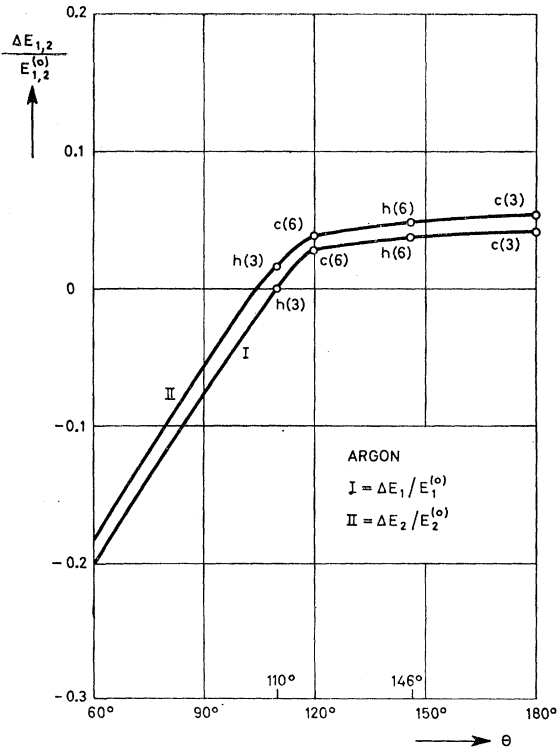


FIG. 3. Comparison between the relative first- and second-order three-body interactions for triangles $a=b=1$, c (units of nearest-neighbor distance) of solid argon ($\beta R=2.4$) as a function of the angle θ between the sides a and b . The nine different fcc and hcp triangles (Table I) are also indicated.

$(\beta R, \theta)$ of argon atoms. Indicated are also the points of the curve referring to the nine hcp and the nine fcc triangles of Table I.

Three main conclusions can be drawn from the figure:

(A) $\Delta E_1/E_1^{(0)} \approx \Delta E_2/E_2^{(0)}$ for all triangles considered. This has the consequence that we may write the total (first-order plus second-order) relative three-body interactions for each triangle as follows:

$$\Delta E/E^{(0)} \equiv (\Delta E_1 + \Delta E_2)/(E_1^{(0)} + E_2^{(0)}) \approx \Delta E_1/E_1^{(0)} \approx \Delta E_2/E_2^{(0)}. \quad (29)$$

The following two possibilities are then to be distinguished:

(A₁) $E^{(0)} = E_1^{(0)} + E_2^{(0)} < 0$. This means that the total pair interactions between the atoms on the triangle are *attractive*. This situation applies for *van der Waals crystals*, such as those of the rare gases. Since $E_1^{(0)} > 0$, $E_2^{(0)} < 0$, we see that in this case ΔE has the same sign as ΔE_2 , and we conclude:

The stability of rare-gas crystals is determined by two-body interactions and by three-body interactions in *second* order of perturbation theory, i.e., the same order as the van der Waals forces themselves.

(A₂) $E^{(0)} = E_1^{(0)} + E_2^{(0)} > 0$, implying that the total

pair interactions between the atoms on the triangle are *repulsive*. This situation applies for *alkali-halide crystals*, where it is to be remembered that we have subtracted the electrostatic interactions between the ionic charges. The reason why $E^{(0)}$ has now reversed its sign compared with van der Waals crystals is because the Madelung energy has *compressed* the crystal to the extent that the closest ions repel each other. In this case the total three-body energy ΔE has the same sign as ΔE_1 , the first-order effect, and we conclude:

The stability of alkali-halide crystals is determined by two-body interactions and by three-body interactions in *first* order of perturbation theory.

(B) *First-order* three-body exchange interactions favor triangles with *small* opening θ ;

(C) *Second-order* three-body exchange interactions favor triangles with *large* opening θ .

On the basis of these properties of three-body interactions the stability problem for rare-gas solids can be solved. Since the pair energy, $E^{(0)}$, for each isosceles triangles is negative, ΔE has the same sign as ΔE_2 , i.e., the total three-body effect *favours the face-centered-cubic configuration for rare-gas crystals*. To estimate the energy difference between the hcp and fcc structures relative to the pair energy of the crystal we proceed in the following way. Let ϵ denote the value of the pair energy at the equilibrium nearest-neighbor distance, R , in the lattice, and let Δ_θ denote the total (first- plus second-order) three-body energy for an isosceles triangle with opening θ . Then 3ϵ is the value of $E^{(0)}$ for $\theta=60^\circ$; for the other isosceles triangles it is sufficiently accurate to calculate $E^{(0)}$ on the basis of a Lennard-Jones (12,6) potential. The values of $E^{(0)}$ at $\theta=60^\circ, 90^\circ, 120^\circ, 146^\circ$, and 180° are then $3\epsilon, 3\epsilon(0.745), 3\epsilon(0.691), 3\epsilon(0.684)$, and $3\epsilon(0.677)$, respectively.

To calculate Δ_θ we note that, for the isosceles triangles considered, $E_2^{(0)}$ is practically precisely $-2E_1^{(0)}$. This gives

$$\left(\frac{\Delta E_1 + \Delta E_2}{E_1^{(0)} + E_2^{(0)}} \right) E^{(0)} = \left(-\frac{\Delta E_1}{E_1^{(0)}} + 2\frac{\Delta E_2}{E_2^{(0)}} \right) E^{(0)}. \quad (30)$$

From Fig. 3 we determine values of Δ_θ of $-0.48\epsilon; -0.1341\epsilon; \approx 0; 0.1244\epsilon; 0.1231\epsilon; \text{ and } 0.1219\epsilon$ for $\theta=60^\circ, 90^\circ, 110^\circ, 120^\circ, 146^\circ$, and 180° , respectively. By using lattice sums for the hexagonal and cubic structures we find that the total pair-energy of these crystals is the same to within $10^{-2}\%$ and equal to $8.4\epsilon N$, where N is the total number of atoms in the solid.

To determine the total three-body energy of the hcp and fcc structures we sum over all isosceles triangles with two atoms nearest neighbors of the third one. There are 66 of such triangles formed by a central atom and any two of its 12 nearest neighbors. In the fcc structure there are 24 triangles at $\theta=60^\circ$, 12 at 90° , 24 at 120° , and 6 at 180° . In summing the three-body

energy over the crystals, it has to be noted that every equilateral triangle is counted three times in the summation, all other triangles only once. We obtain for the cohesive energy, E_{coh} , of the two structures

$$(E_{\text{coh}})_{\text{fcc}}/N = 8.4\epsilon + 8\Delta_{60} + 12\Delta_{90} + 24\Delta_{120} + 6\Delta_{180}, \quad (31)$$

and

$$(E_{\text{coh}})_{\text{hcp}}/N = 8.4\epsilon + 8\Delta_{60} + 12\Delta_{90} + 3\Delta_{110} + 18\Delta_{120} + 6\Delta_{146} + 3\Delta_{180}. \quad (32)$$

Hence, the relative difference is

$$\frac{(E_{\text{coh}})_{\text{fcc}} - (E_{\text{coh}})_{\text{hcp}}}{8.4\epsilon N} = \frac{6\Delta_{120} + 3\Delta_{180} - (3\Delta_{110} + 6\Delta_{146})}{8.4\epsilon}. \quad (33)$$

By substituting the values for Δ_{θ} , given earlier, we find

$$\frac{(E_{\text{coh}})_{\text{fcc}} - (E_{\text{coh}})_{\text{hcp}}}{8.4\epsilon N} = 0.044. \quad (34)$$

Since $\epsilon < 0$, this implies that the face-centered cubic lattice is more stable than the hexagonal close-packed configuration for solid argon by about 4% of the pair cohesive energy, thus largely exceeding the 0.01% difference in the pair energy which favors the hcp structure. If we take, in first approximation, only the difference between 3 fcc triangles at $\theta = 120^\circ$ and 3 hcp triangles at $\theta = 110^\circ$ [Eq. (6)], then we find the same value to within 0.1%. This shows again, as was noted earlier, that the *essential stabilizing factor* in going from the hcp to the fcc structure is the transition of three triangles from $\theta = 110^\circ$ to $\theta = 120^\circ$.

COHESIVE ENERGY AND ENERGY OF VACANCY FORMATION FOR THE FCC AND HCP STRUCTURES

It is important to compare also the total cohesive energies of the fcc and hcp configurations for solid argon. We find directly, from (31) and (32),

$$\begin{aligned} (E_{\text{coh}})_{\text{fcc}} &= 8.4N\epsilon(1 - 0.206), \\ (E_{\text{coh}})_{\text{hcp}} &= 8.4N\epsilon(1 - 0.251), \end{aligned} \quad (35)$$

implying that the cohesive energies for the cubic and hexagonal structures are decreased in absolute value by 21 and 25%, respectively, because of three-body interactions. The magnitude of this effect is surprising, since it is generally believed that the values of intermolecular potential parameters determined from gas data are in good agreement with a pair-potential interpretation of the cohesive energies of rare-gas solids.^{39,40}

It appears, however, that the three-body component of the cohesive energy is *extremely sensitive* to the precise

values of $\Delta E/E^{(0)}$ for *small* values of θ , whereas the stability of the cubic configuration is not sensitive at all in this region. For example, if we decrease $\Delta E_2/E_2^{(0)}$ at $\theta = 60^\circ$ by 10% from 0.18 to 0.16, and at $\theta = 90^\circ$ from 0.06 to 0.05, then we obtain with (30), (31), and (32), for the cohesive energies

$$\begin{aligned} (E_{\text{coh}})_{\text{fcc}} &= 8.4N\epsilon(1 - 0.028), \\ (E_{\text{coh}})_{\text{hcp}} &= 8.4N\epsilon(1 - 0.073), \end{aligned}$$

so that with a small change the three-body part of the cohesive energy for the fcc and hcp structures decreases to about 3 and 7%, respectively. This result shows that the difference in three-body energy between the two lattices may be comparable with the three-body component of the cohesive energies themselves. Our present precision in the evaluation of some of the basic integrals for small values of θ does not seem to exclude definitely this possibility.

Another quantity of special interest in this connection is the *energy of vacancy formation* in solid argon. Foreman and Lidiard⁴¹ have recently compared experimental data on the specific heat of solid argon for temperatures between 40°K and the melting point with theoretical results obtained on the basis of a lattice dynamical calculation using the anharmonic Einstein model. The difference between the two curves was ascribed to vacancies in the lattice, which allows the calculation of the free energy of vacancy formation. They found a considerable discrepancy with theoretical results by Nardelli and Repanai Chiarotti⁴² based on two-body interactions between the atoms, in that Foreman and Lidiard's values are *smaller* by a factor of about 1.7 than the two-body results. A preliminary analysis³⁵ of this effect on the basis of three-body interactions has been given earlier.⁴³

We consider a fcc crystal of N argon atoms without vacancies, and compare its cohesive energy with that of a crystal with N atoms plus one vacancy; the difference is then the (static) energy of vacancy formation, E_{vac} . For the crystal without vacancies, we have, from (31),

$$E_{\text{coh}} = N[8.4\epsilon + 8\Delta_{60} + 12\Delta_{90} + 24\Delta_{120} + 6\Delta_{180}]. \quad (31')$$

In the case of N atoms plus one vacancy we lose, first of all, the two-body energy of one atom, 8.4ϵ . To determine the three-body interactions, we calculate these first with an atom at the site of the vacancy (i.e., a system of $N+1$ atoms without vacancies) and then subtract *all* three-body interactions which involve the atom at the vacancy. The result for the (static) cohesive energy, E_{coh}' , for N atoms plus one vacancy is

$$E_{\text{coh}}' = (N-1)8.4\epsilon + (N+1)[8\Delta_{60} + 12\Delta_{90} + 24\Delta_{120} + 6\Delta_{180}] - [24\Delta_{60} + 36\Delta_{90} + 72\Delta_{120} + 18\Delta_{180}]. \quad (31'')$$

³⁹ E. R. Dobbs and G. P. Jones, Rept. Progr. Phys. **20**, 516 (1957).

⁴⁰ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), Chap. 2.

⁴¹ A. J. E. Foreman and A. B. Lidiard, Phil. Mag. **8**, 97 (1963).

⁴² G. F. Nardelli and A. Repanai Chiarotti, Nuovo Cimento **18**, 1053 (1960).

⁴³ Equations (3) and (4) of Ref. 35 are inaccurate because of the omission of additional three-body interactions.

The (static) vacancy energy, E_{vac} , is then

$$E_{\text{vac}} \equiv E_{\text{coh}} - E_{\text{coh}}' = 8.4\epsilon + 16\Delta_{60} + 24\Delta_{90} + 48\Delta_{120} + 12\Delta_{180} \quad (36)$$

Comparison with (31) shows that the three-body component of the vacancy energy is just *twice* that of the cohesive energy per atom for the perfect crystal. From (35) we find, therefore, that $E_{\text{vac}} = 8.4\epsilon(1 - 0.412)$, whereas the two-body value would be 8.4ϵ . For the ratio between the two-body vacancy energy and (36) we obtain $1/0.588 = 1.70$, in excellent agreement with the value determined by Foreman and Lidiard.

It should be noted that E_{vac} , like the cohesive energy, exhibits extreme sensitivity with respect to the values of $\Delta E_2/E_2^{(0)}$ for small θ : If we take again 0.16 instead of 0.18 for the relative second-order effect at $\theta = 60^\circ$, then the vacancy energy increases to $8.4\epsilon(1 - 0.056)$ and the above ratio becomes 1.06 instead of 1.70. Consequently, *if* Foreman and Lidiard's analysis is correct, then also the cohesive energy of the fcc lattice has a considerable three-body component.

CONCLUDING REMARKS

We have found that the stability of the face-centered-cubic configuration for rare-gas crystals depends primarily on the *type* of curve for $\Delta E/E^{(0)}$ as a function of the opening, θ , of the isosceles triangles formed by a central atom and any two of its nearest neighbors in the crystal. Moreover, the difference in three-body cohesive energy between the fcc and hcp structures changes very little even if we decrease the magnitude of $\Delta E/E^{(0)}$ at $\theta = 60^\circ$ by 40%, whereas the three-body components of the cohesive energy and the energy of vacancy formation decrease by almost an order of magnitude.

One then has to make sure that this type of behavior for $\Delta E/E^{(0)}$ is not induced by the specific choice of a Gaussian distribution for the effective charges. The answer to this question is twofold. First of all, a Gaussian distribution is in very good agreement with the two-body potential between neon atoms, with the same value of the parameter β for large and small interatomic distances.²⁶ In addition, it appears that the outer part of a Hartree-Fock charge distribution for argon atoms can be fitted with a Gaussian function; the resulting value for β is the same to within five percent as that determined from long-range interactions.²⁸ Secondly, we have compared in Fig. 2 the $\Delta E_2/E_2^{(0)}$ dependence on θ with that of the Axilrod-Teller effect, magnified twenty times. In this way, good agreement is obtained at $\theta = 60^\circ$ and 180° ; the differences for intermediate values of θ are the result of exchange, and not of the Gaussian distribution.

The same comparison applies for the Rosen-Shostak first-order three-body interactions between three helium atoms.^{24,25} Rosen found that for an equilateral triangle and a linear array of helium atoms, $\Delta E_1/E_1^{(0)}$ can be represented by $A \exp[-a(R_{ab} + R_{ac} + R_{bc})]$ with

$A = -1.15$; $a = 0.33$ and $A = +9.8$; $a = 0.66$ for these two cases, respectively (all distances are expressed in atomic units). If we take $R_{ab} = R_{ac} = 1.98$ a.u. ($= 1 \text{ \AA}$), then $\Delta E_1/E_1^{(0)}$ is equal to -18% at 60° and $+6.6\%$ at 180° , in excellent agreement with the Gaussian $\Delta E_1/E_1^{(0)}$ values for argon. Since the Rosen-Shostak effect is due to exchange, its values for intermediate θ must lie close to those given by the Gaussian model. It appears, therefore, that the Gaussian distribution plays a "neutral" role in determining the θ dependence of the relative three-body interactions.

Upon increasing the value of the dimensionless parameter βR , i.e., upon going to lighter rare-gas atoms or expanding the crystal, the positive part of the $\Delta E/E^{(0)}$ curve approaches the horizontal axis. For solid helium (He^4), the differences between the three-body energies of the fcc and hcp lattices disappear completely, and the hcp structure becomes more stable because of its more negative two-body energy. The transition to face-centered cubic structure observed by Dugdale and Simon⁴⁴ may, consequently, be interpreted in terms of two-body interactions alone.⁴⁴ Recently, a third solid phase of He^4 was found which is probably body-centered cubic.⁴⁵

Although the difference in cohesive energy between the two close-packed configurations of rare-gas crystals was found to amount to as much as 4%, its absolute value is still very small, namely, of the order of 0.1 kcal/mole for the heavier atoms. Solid neon appears to be a limiting case and it is therefore not excluded that it could be observed in hexagonal packing by special crystallization techniques. It is of interest to note that recently Meyer, Barrett, and Haasen⁴⁶ have observed a *metastable* hexagonal argon phase which sometimes occurs in polycrystalline blocks frozen from a bath of liquid, with a high density of stacking faults. Upon the addition of small amounts of nitrogen, the hexagonal phase becomes stable near the melting point of the crystal.

A large number of other van der Waals crystals are known to crystallize in close-packed structures. Some of them, for example nitrogen and carbon monoxide, exhibit a transition from fcc to hcp with increasing temperature. The same general type of three-body exchange interactions must be expected to play a role for stability in those solids, supplemented by orientational two-body forces (e.g., due to electric quadrupoles). Kihara⁴⁷ has recently built experimental models of such molecules and shown that they crystallize in the observed structure for sufficiently strong quadrupole moments.

⁴⁴ J. S. Dugdale and F. E. Simon, Proc. Roy. Soc. (London) **A218**, 291 (1953).

⁴⁵ Cf. A. F. Schuch, W. C. Overton, Jr., and R. Brout, Phys. Rev. Letters **10**, 429 (1963).

⁴⁶ Lothar Meyer, C. S. Barrett, and P. Haasen (to be published).

⁴⁷ T. Kihara, Acta Cryst. **16**, 1119 (1963).

No attempt has been made in the present analysis to extend the calculations beyond second-order perturbation effects, nor to include simultaneous interactions between more than three atoms. The reason is, first of all, the prohibitive complexity of higher order calculations and, further, the belief that such a double-series expansion (in the number of simultaneously interacting atoms on one hand, and in orders of perturbation theory on the other hand) must converge rapidly in order to render an "atomic" description of van der Waals crystals at all valid. The comparison with the Axilrod-Teller third-order effect given in Fig. 2 supports this supposition. The relative three-body interactions between rare-gas atoms are considerable at short range; this result seems to be indirectly confirmed by the recently established chemical reactivity of the heavy rare gases, indicating that the closed electron shells are less stable than was originally believed.

We found that the rare-gas crystals are constructed according to a minimum-energy principle involving two-body interactions and triplet energies which follow simple symmetry principles. These principles may be illustrated by considering a central atom in the crystal and its twelve nearest neighbors, of which six are on a

hexagon in the central plane, and three on triangles above and below this plane. In the hcp structure the two triangles have the same orientation, whereas in the fcc configuration one triangle is rotated by 60° with respect to the other. This rotation implies a very small loss in two-body energy, but a substantial gain in three-body interactions, involving the transition of three hcp triangles at $\theta=110^\circ$ to fcc triangles with slightly larger opening, namely 120° .

In a following publication the stability of alkali-halide crystals will be analyzed on the same basis.

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APPENDIX I

Linear Relations between Auxiliary Functions \mathcal{A} to \mathcal{H} [Eqs. (9)–(16)] and Basic Integrals K to S [Eqs. (17)–(25)]

$$\mathcal{A}(x) = 1/x^2 + 2L^2(x) + (2^{1/2}/x)L(x/2^{1/2}) + N(x) - 4L(x)/x - 4M(x),$$

$$\mathcal{B}(x) = 1 + 1/x^2 + (2/x)(2/\pi)^{1/2} + 2K(\frac{1}{2}x) + 2L^2(\frac{1}{2}x) - (4/x)L(\frac{1}{2}x) - 4R(\frac{1}{2}x).$$

$$\mathcal{C}(x_1, x_2; \alpha) = [1/x_1 - L(x_1)][1/x_2 + L(x_2/2^{1/2})/2^{1/2} - 2L(x_2)] + [1/x_2 - L(x_2)][L(x_1/2^{1/2})/2^{1/2} - L(x_1)] \\ + (1/\pi^{3/2})[O(x_1, x_2; \alpha) - P(x_1, x_2; \alpha) - P(x_2, x_1; \alpha) + Q(x_2, x_1; \alpha)],$$

where $\alpha = \sphericalangle x_1, x_2$.

$$\mathcal{D}(x_1, x_2; \alpha) = 1/x_1^2 + K(x_1) + 2L(x_1)L(x_2) + (2^{1/2}/x_1)L(x_2/2^{1/2}) \\ + N(x_2) - (2/x_1)[L(x_1) + L(x_2)] - 2M(x_2) - (2/\pi^{3/2})P(x_1, x_2; \alpha),$$

where $\alpha = \sphericalangle x_1, x_2$.

$$\mathcal{E}(x_1, x_2, x_3) = 1/x_1x_2 - L(x_3)L(x_3/2^{1/2})/2^{1/2} + L(x_1)[L(x_3) - 1/x_2] + L(x_2)[L(x_3) - 1/x_1] + [L(x_3) \\ - (x_1 + x_2)/x_1x_2][L(x_3) - L(x_3/2^{1/2})/2^{1/2}] + \pi^{3/2}[O(x_1, x_2; \sphericalangle x_1, x_2) \\ - P(x_1, x_2; \sphericalangle x_1, x_3) - P(x_2, x_3; \sphericalangle x_2, x_3) + S(x_3)].$$

$$\mathcal{F}(x_1, x_2, x_3) = [1/x_2 - L(x_2)][1/x_1 - 2L(x_1/2) + (2/\pi)^{1/2}] + [L(\frac{1}{2}x_1) - 1/x_1][L(x_3) - L(x_3/2^{1/2})/2^{1/2}] \\ - R(x_3) + \pi^{-3/2}[O(x_1/2, x_3; \sphericalangle x_1/2, x_3) - P(x_1/2, x_3; \sphericalangle x_1/2, x_3) + Q(x_3, 0)].$$

$$\mathcal{G}(x_1, x_2, x_3) = 1/x_1^2 + K(\frac{1}{2}x_1) + K(x_2) + N(x_3) + 2L(\frac{1}{2}x_1)[L(x_2) - 1/x_1] + 2/x_1[L(x_3/2^{1/2})/2^{1/2} - L(x_2)] \\ - (2/\pi^{3/2})[P(x_1/2, x_3; \sphericalangle x_1/2, x_3) + P(x_2, x_3; \sphericalangle x_2, x_3)].$$

$$\mathcal{H}(x_1, x_2, x_3, (x_4, x_5, x_6)) = [L(\frac{1}{2}x_2) - 1/x_2][L(\frac{1}{2}x_1) + L(x_6) - L(x_3/2^{1/2})/2^{1/2} - 1/x_1] \\ + [L(x_6) - 1/x_1][L(x_3) - L(x_4/2^{1/2})/2^{1/2}] + \pi^{-3/2}[O(x_1/2, x_3; \sphericalangle x_1/2, x_3) \\ - P(x_1/2, x_4; \sphericalangle x_1/2, x_4) - P(x_3, x_5; \sphericalangle x_3, x_5) + Q(x_4, x_5; \sphericalangle x_4, x_5)].$$

The variables $x_1, x_2, x_3, x_4, x_5, x_6$ have the following meaning: $\mathcal{H}(\beta R_{ac}, \beta R_{bc}, \beta R_{b(ac)})$:

x_1	x_2	x_3	x_4	x_5	x_6
βR_{ac}	βR_{bc}	$\beta R_{b(ac)}$	$\beta R_{(ac)(bc)}$	$\beta R_{(ab)(ac)}$	$\beta R_{c(ab)}$

For the remaining five \mathcal{H} functions the variables are found by permutations, as explained in the text of the paper

APPENDIX II

(A) Asymptotic Series Expansions Used for the Evaluation of the Basic Integrals

$$\begin{aligned}
 K(x) &\equiv \frac{2}{x} e^{-x^2} \int_0^x e^{t^2} dt \approx \frac{1}{x^2} + \frac{1}{2x^4} + \frac{3}{4x^6} + \dots + \frac{(2n-3)!!}{2^{n-1}x^{2n}} + \dots, \\
 L(x) &\equiv \frac{2}{\pi^{1/2}} \frac{1}{x} \int_0^x e^{-t^2} dt \equiv \frac{\operatorname{erf} x}{x} \approx \frac{1}{x} - \frac{e^{-x^2}}{x^2 \pi^{1/2}} \left[1 - \frac{1}{2x^2} + \frac{1 \times 3}{(2x^2)^2} + \dots + \frac{(-1)^{n-1} (2n-3)!!}{(2x^2)^{n-1}} + \dots \right], \\
 M(x) &= \frac{e^{-x^2}}{x} \int_0^x e^{u^2} \left(\operatorname{erf} \frac{u}{2^{1/2}} \right)^2 du \approx \frac{1}{2} K(x) - \frac{2^{3/2} e^{-x^2} / 2}{\pi^{1/2} x^3} \left(1 + \frac{7}{x^2} + \frac{27}{x^4} + \frac{321}{x^6} + \dots \right), \\
 N(x) &\equiv \frac{2}{x \pi^{1/2}} \int_0^\infty \left\{ (e^{-[(u-x)^2+u^2]} - e^{-[(u+x)^2+u^2]}) \int_0^u e^{t^2} dt \right\} du \approx \frac{1}{x^2} + \frac{1}{x^4} + \frac{3}{x^6} + \frac{3 \times 5}{x^8} + \dots + \frac{(2n-3)!!}{x^{2n}} + \dots, \\
 S(x) &\equiv \frac{4}{x} \int_0^\infty (e^{-(u-x)^2} - e^{-(u+x)^2}) \left(\int_0^u e^{-t^2} dt \right)^2 du \approx \pi^{3/2} K(x) - 2^{5/2} \pi \frac{e^{-x^2} / 2}{x^3} + \dots,
 \end{aligned}$$

and

$$R(x) \equiv 1 - x^2 L^2(x) + (2/\pi^{1/2}) [L(x 2^{1/2}) - e^{-x^2} L(x)] \approx \frac{2^{1/2}}{\pi^{1/2}} \frac{1}{x} - \frac{e^{-x^2}}{x^3 \pi^{1/2}} + \frac{3}{2\pi^{1/2}} \frac{e^{-x^2}}{x^5} + \dots$$

(B) Double-Series Development Used for the Evaluation of $Q(u, v, \alpha)$, for Large u and v

$$\begin{aligned}
 Q(u, v, \alpha) &\equiv \int_0^\infty \int_0^{2\pi} \int_0^\pi (u^2 + r^2 - 2ur \sin \theta \sin \varphi)^{-1/2} \cdot (v^2 + r^2 - 2vr \sin \theta \sin(\varphi + \alpha))^{-1/2} \\
 &\quad \times \operatorname{erf}[(u^2 + r^2 - 2ur \sin \theta \sin \varphi)^{1/2}] \cdot \operatorname{erf}[(v^2 + r^2 - 2vr \sin \theta \sin(\varphi + \alpha))^{1/2}] r^2 e^{-r^2} \sin \theta d\theta d\varphi dr \\
 &\approx 2 \sum_{n+m=\text{even}} \sum \frac{(2n-1)!! (2m-1)!!}{(2n)!! (2m)!!} \frac{(n+m)!!}{(n+m+1)!!} \int_0^{2\pi} \sin^n \varphi \sin^m(\alpha + \varphi) \sum_{i=0}^l \int_{r_i}^{r_{i+1}} \left(\frac{2ur}{u^2 + r^2} \right)^n \left(\frac{2vr}{v^2 + r^2} \right)^m \\
 &\quad \times \frac{r^2 e^{-r^2} dr}{(u^2 + r^2)^{1/2} (v^2 + r^2)^{1/2}} \cdot \operatorname{erf}(u - r_i) \operatorname{erf}(v - r_i),
 \end{aligned}$$

where $u \geq v$,

$$0 = r_0 < r_1 < \dots < r_i < r_{i+1} < \dots < r_l = v - \epsilon,$$

and ϵ is a positive small number. The derivation of these series expansions, together with numerical details and error estimates, is given in a separate report.³⁸

APPENDIX III

Summary of Some Numerical Results

In the following tables a number of numerical results for the relative first- and second-order three-body interactions are given. Tables II and III are associated with Figs. 1 and 2, respectively; in Table IV values for the auxiliary

TABLE II. Numerical results for relative first-order, three-body interactions $\Delta E_1/E_1^{(0)}$ for isosceles triangles of argon atoms ($\beta R = 2.4$) and of xenon atoms ($\beta R = 2.0$), as a function of the angle θ between the sides R_{ab} and R_{ac} .

θ	60°	90°	109°28'	120°	146°27'	180°
Argon	-0.200	-0.075	0	0.027	0.038	0.041
Xenon	-0.214	-0.075	+0.008	0.051	0.076	0.098

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 TABLE III. Numerical results for relative second-order, three-body interactions $\Delta E_2/E_2^{(0)}$ for isosceles triangles of argon atoms ($\beta R = 2.4$), as a function of the angle θ between the sides R_{ab} and R_{ac} of the triangle. The relative contributions of diatomic exchange and triatomic exchange are also given.

θ	60°	90°	109°28'	120°	146°27'	180°
$E_2/E_2^{(0)}$ { diatomic	+0.280	+0.140	+0.086	+0.081	+0.072	+0.070
{ triatomic	-0.458	-0.192	-0.070	-0.035	-0.015	-0.011
{ total	-0.178	-0.052	+0.016	+0.046	+0.057	+0.059

TABLE IV. Numerical values for the auxiliary functions.

A. \mathcal{A} and \mathcal{B} [Eqs. (9) and (10) of the text]; $x = \beta R_{ab} = \beta R_{ac} = 2.5$.											
θ	x_1^2 $x_1 = \beta R_{bc}$	Numerical value $\times 10^3$ of $\mathcal{A}(x_1)$	Numerical value $\times 10^6$ of $\mathcal{B}(x_1)$	Function	θ	$(x_1/x)^2$	$(x_2/x)^2$	$(x/x)^2$	Numerical value $\times 10^6$		
60°	1	21 561	38 572	$2\Delta_{bc}^2 \mathcal{E}(x_1, x_2, x_3)$ $x_1 = \beta R_{ac}$ $x_2 = \beta R_{ab}$ $x_3 = \beta R_{a(bc)}$	60°	1	1	3/4	-312		
90°	2	1973	1031		90°	1	1	1/2	+30		
109°28'	8/3	647	118		109°28'	1	1	1/3	+12		
120°	3	420	38		120°	1	1	1/4	+4		
146°27'	11/3	191	5		146°27'	1	1	1/12	+1		
180°	4	142	1		180°	1	1	0	<1		
B. \mathcal{C} and \mathcal{D} [Eqs. (11) and (12) of the text]; $x = \beta R_{ab} = \beta R_{ac} = 2.5$.											
Function	θ	$(x_1/x)^2$	$(x_2/x)^2$	b^2 $b = \cos \alpha$	Numerical value $\times 10^6$						
$4\mathcal{C}(x_1, x_2, \alpha)$ $x_1 = \beta R_{ac}$ $x_2 = \beta R_{bc}$ $\alpha = \angle bca$	60°	1	1	1/4	64	$4\Delta_{ab}^2 \mathcal{F}(x_1, x_2, x_3)$ $x_1 = \beta R_{ac}$ $x_2 = \beta R_{ab}$ $x_3 = \beta R_{b(ac)}$	60°	1	1	3/4	441
	90°	1	2	1/2	6		90°	1	1	5/4	76
	109°28'	1	8/3	2/3	1		109°28'	1	1	19/12	18
	120°	1	3	3/4	<1		120°	1	1	7/4	7
	146°27'	1	11/3	11/12	<1		146°27'	1	1	25/12	+2
	180°	1	4	1	<1		180°	1	1	9/4	-4
$2\mathcal{C}(x_1, x_2, \alpha)$ $x_1 = \beta R_{ab}$ $x_2 = \beta R_{ac}$ $\alpha = \angle cab$	60°	1	1	1/4	32	$4\Delta_{ab}^2 \mathcal{F}(x_1, x_2, x_3)$ $x_1 = \beta R_{ab}$ $x_2 = \beta R_{bc}$ $x_3 = \beta R_{c(ab)}$	60°	1	1	3/4	441
	90°	1	1	0	7		90°	1	2	5/4	81
	109°28'	1	1	1/9	4		109°28'	1	8/3	19/12	24
	120°	1	1	1/4	3		120°	1	3	7/4	13
	146°27'	1	1	25/36	<1		146°27'	1	11/3	25/12	3
	180°	1	1	1	<1		180°	1	4	9/4	2
$2\Delta_{ab}^2 \mathcal{D}(x_1, x_2, \alpha)$ $x_1 = \beta R_{ac}$ $x_2 = \beta R_{c(ab)}$ $\alpha = \angle ac(ab)$	60°	1	3/4	3/4	3052	$4\Delta_{bc}^2 \mathcal{F}(x_1, x_2, x_3)$ $x_1 = \beta R_{bc}$ $x_2 = \beta ac$ $x_3 = \beta R_{a(bc)}$	60°	1	1	3/4	441
	90°	1	5/4	4/5	1607		90°	1/2	1	1/2	40
	109°28'	1	19/12	49/57	938		109°28'	8/3	1	1/3	13
	120°	1	7/4	25/28	884		120°	3	1	1/4	6
	146°27'	1	25/12	289/300	791		146°27'	11/3	1	1/12	1
	180°	1	9/4	1	760		180°	4	1	0	<1
$2\Delta_{ab}^2 \mathcal{D}(x_1, x_2, \alpha)$ $x_1 = \beta R_{bc}$ $x_2 = \beta R_{c(ab)}$ $\alpha = \angle bc(ab)$	60°	1	3/4	3/4	3052	$2\Delta_{ab}^2 \Delta_{bc} \mathcal{G}(x_1, x_2, x_3)$ $x_1 = \beta R_{ac}$ $x_2 = \beta R_{a(bc)}$ $x_3 = \beta R_{(bc)(ac)}$	60°	1	3/4	1/4	6032
	90°	2	5/4	9/10	1167		90°	1	1/2	1/4	2510
	109°28'	8/3	19/12	18/19	442		109°28'	1	1/3	1/4	1140
	120°	3	7/4	3/28	354		120°	1	1/4	1/4	712
	146°27'	11/3	25/12	33/100	195		146°27'	1	1/12	1/4	396
	180°	4	9/4	1	150		180°	1	0	1/4	339
$2\Delta_{bc}^2 \mathcal{D}(x_1, x_2, \alpha)$ $x_1 = \beta R_{ac}$ $x_2 = \beta R_{a(bc)}$ $\alpha = \angle ca(bc)$	60°	1	3/4	3/4	3052	$2\Delta_{ab}^2 \Delta_{bc} \mathcal{G}(x_1, x_2, x_3)$ $x_1 = \beta R_{bc}$ $x_2 = \beta R_{c(ab)}$ $x_3 = \beta R_{(ac)(ab)}$	60°	1	3/4	1/4	6032
	90°	1	1/2	1/2	300		90°	1	5/4	1/2	1228
	109°28'	1	1/3	1/3	86		109°28'	1	19/12	2/3	409
	120°	1	1/4	1/4	56		120°	1	7/4	3/4	222
	146°27'	1	1/12	1/12	12		146°27'	1	25/12	11/12	74
	180°	1	0	1	7		180°	1	9/4	1	41
C. \mathcal{E} , \mathcal{F} , \mathcal{G} , and \mathcal{H} [Eqs. (13)–(16) of the text]; $x = \beta R_{ab} = \beta R_{ac} = 2.5$.											
Function	θ	$(x_1/x)^2$	$(x_2/x)^2$	$(x/x)^2$	Numerical value $\times 10^6$						
$4\Delta_{ab}^2 \mathcal{E}(x_1, x_2, x_3)$ $x_1 = \beta R_{ac}$ $x_2 = \beta R_{bc}$ $x_3 = \beta R_{c(ab)}$	60°	1	1	3/4	-624	$4\Delta_{ab}^2 \Delta_{bc} \mathcal{H}(x_1, x_2, x_3)$ $x_1 = \beta R_{ac}$ $x_2 = \beta R_{ab}$ $x_3 = \beta R_{b(ac)}$	60°	1	1	3/4	1225
	90°	1	2	5/4	-360		90°	1	1	5/4	488
	109°28'	1	8/3	19/12	-340		109°28'	1	1	19/12	250
	120°	1	3	7/4	-330		120°	1	1	7/4	155
	146°27'	1	11/3	25/12	-324		146°27'	1	1	25/12	73
	180°	1	4	9/4	-320		180°	1	1	9/4	51

TABLE IV (continued)

Function	θ	$(x_1/x)^2$	$(x_2/x)^2$	$(x/x)^2$	Numerical value $\times 10^6$	Function	θ	$(x_1/x)^2$	$(x_2/x)^2$	$(x/x)^2$	Numerical value $\times 10^6$
$4\Delta_{ab}^2\Delta_{bc}\mathcal{C}(x_1, x_2, x_3)$	60°	1	1	3/4	1225	$4\Delta_{ab}^2\Delta_{bc}\mathcal{C}(x_1, x_2, x_3)$	60°	1	1	3/4	+1225
	90°	1	2	5/4	+232		90°	2	1	1/2	-24
$x_1 = \beta R_{ac}$	109°28'	1	8/3	19/12	-13	$x_1 = \beta R_{bc}$	109°28'	8/3	1	1/3	-65
$x_2 = \beta R_{bc}$	120°	1	3	7/4	-41	$x_2 = \beta R_{ac}$	120°	3	1	1/4	-115
$x_3 = \beta R_{b(ac)}$	146°27'	1	11/3	25/12	-51	$x_3 = \beta R_{a(bc)}$	146°27'	11/3	1	1/12	-77
	180°	1	4	9/4	-57		180°	4	1	0	-67

functions \mathcal{G} - \mathcal{C} [Eqs. (9)-(16) of the text] are collected for isosceles triangles abc of argon atoms. To simplify the notation the dimensionless nearest-neighbor distance $\beta R_{ab} = \beta R_{ac}$ is represented by x ; the numerical results for the auxiliary functions correspond with $x = 2.5$.

Polar Reflection Faraday Effect in Metals*

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If one reflects plane-polarized light from a nonferromagnetic metal with a magnetic field normal to the reflecting surface, the reflected light is found to have its plane of polarization rotated from that of the incident beam, and is slightly elliptically polarized. This effect is known as the polar reflection Faraday effect (PRFE). The PRFE has been measured for aluminum and silver as a function of wavelength in the range 4150-8000 Å. The equipment to measure this effect to an accuracy of about 2% is described. Detailed studies on aluminum have shown that the PRFE is much less sensitive to the condition of the surface than ordinary optical-constant measurements and the measurements presented appear to be representative of bulk properties. The frequency dependence found for both aluminum and silver can in large part be explained by the simple intra-band theory. Although the theory relates the PRFE to the off-diagonal term of the conductivity tensor, the inconsistency of the many optical measurements of aluminum makes the determination of the off-diagonal conductivity ambiguous. In the case of silver, the real and imaginary parts of the off-diagonal conductivity can be obtained with a fair degree of accuracy.

I. INTRODUCTION

IT has been well known for quite some time that plane-polarized light after reflection from ferromagnetic metals magnetized normal to the reflection plane becomes elliptically polarized with its major axis rotated from the initial polarization direction.¹ The angle of rotation of this magneto-optic Kerr effect is of the order of one degree, and it is caused by the spin-orbit interaction.² Less well known and certainly not as intensely studied experimentally is an experimentally similar effect in nonferromagnetic metals which we call the polar reflection Faraday effect. Plane-polarized light

incident normally on a nonferromagnetic metal surface with a magnetic field normal to the surface, suffers on reflection a small rotation of the plane of polarization and also becomes slightly elliptically polarized. The reason why this effect has not been well studied experimentally is not hard to surmise when one realizes that the angle of rotation is about 10^{-4} deg for a field of 10^8 Oe. The amount of an elliptical polarization is also correspondingly smaller. In a rather remarkable bit of work, especially considering the experimental techniques available at that time, Majorana was apparently the first one to measure the polar reflection Faraday effect, doing so for Al, Ag, Au, Pt, Bi.³ His accuracy was understandably poor but he unquestionably showed the existence of the effect. Later and independently the effect was rediscovered and measured with greater accuracy taking advantage of the more modern techniques available.^{4,5}

* This research is partly based on the Ph.D. dissertation of James C. McGroddy, University of Maryland, 1964.

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