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Perturbation Analysis of Three- and Four-Atom Exchange Interactions in a Gaussian Effective-Electron Model

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An analysis of three- and four-atom interactions of exchange type in first and second orders of perturbation theory is presented, on the basis of an effective-electron model with a Gaussian distribution of charge. The results are then applied to a determination of the three- and four-atom components of the crystal energy for close-packed rare-gas solids. It is found that both the three- and four-atom interactions favor a fcc crystal structure. The magnitude of the four-atom energy relative to the three-atom component for a given atomic species and a given crystalline configuration is essentially a function only of the ratio between the second- and first-order pair interactions for nearest neighbors in the solid. For the most probable range of values of this ratio, the four-atom crystal energy is relatively unimportant. The sum of three- and four-atom crystal energies is found to vary little with the ratio. Calculated values for the stacking-fault energy in solid argon and xenon agree reasonably well with those obtained from observations on thin films of these solids.

I. INTRODUCTION

THE possible importance of simultaneous interactions between more than two atoms or ions for the interpretation of macroscopic properties of dense media (solids, liquids, and compressed gases) has in recent years become a subject of considerable interest in the literature. We have analyzed in previous publications the problem of crystal stability and polymorphism for molecular and ionic solids along these lines, on the assumption that three-atom and three-ion interactions of exchange type in these solids constitute the essential structure-sensitive short-range component of the crystal energy. The solids considered were those formed by rare-gas atoms,[1] alkali halides,[2] and II–VI and III–V compounds,[3] as well as those formed by ionic compounds of composition AX_2.[4] All ions considered are isoelectronic with rare-gas atoms. In adopting an effective-electron approximation with a Gaussian charge distribution for the electrons and in carrying out a perturbation treatment for these interactions in first and second orders, it was found that all observed crystal stability relations can be given a quantitative explanation. General stability rules were formulated for the occurrence of each of a large number of possible structures.

As for a general classification of many-particle (atom or ion) interactions, the above exchange forces refer to the short-range part of the many-atom or many-ion potential. These forces occur already in the lowest orders of perturbation theory, both for atoms or ions with closed and with open shells of electrons in the ground state. In case of open-shell ions, the so-called "superexchange" forces in solids of certain d-electron oxides belong typically to this category. In addition to these many-particle interactions, also those which are not of exchange type occur in principle. The best-known example is the classical induction energy for an atom in a field of electrostatic point charges. Further, the third-order so-called "triple-dipole" interactions suggested by Axilrod and Teller[5,6] and by Kihara[7] are representative for this class of nonexchange, long-range, many-atom forces. Such long-range interactions between atoms are expected to dominate over the short-range components in case the density of the system is relatively low, e.g., in the analysis of third virial coefficients for gases.

The effect of (long- or short-range) three-atom interactions on different properties of dense rare gases has recently been discussed by many authors. Among these we mention, in particular, an analysis of solid-state properties of argon by Götze and Schmidt,[8] by Rossi and Danon,[9] and by Klein and Munn[10]; of the stacking-fault energy in solid argon by Plishkin and Greenberg[11] and by Bullough, Glyde, and Venables[12]; of the vacancy energy in solid argon by Glyde[13] and by Peterson, Batchelder, and Simmons[14]; of the third virial coefficient of argon by Graben, Present, and McCulloch[15] and by Sherwood, De Rocco, and Mason[16]; and of the isotopic separation factor of liquid argon by Rowlinson.[17] Dis-

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cussions of more general aspects of many-atom contributions to the intermolecular potential in dense media are given in recent review articles by Mason and Monchick,[18] and by Sinanoğlu,[19] as well as in a forthcoming book by Margenau and Kestner.[20] A particular component of many-atom forces of the charge-transfer type has been analyzed by Murrell, Randič, and Williams,[21] in connection also with rare-gas crystal stability.

A few words should be said concerning the information on many-atom interactions which can in principle be obtained from an analysis of various properties of dense media and from comparison with experimental data. The analysis of most properties directly involves two-body as well as many-body components of the energy; a separation of many-atom components necessitates, therefore, accurate knowledge of the "pure" pair potential between the atoms. Generally, however, the assumed pair potential is already an "effective" interaction between the atoms, determined from a combination of low- and high-density data (e.g., from second virial coefficients together with solid-state properties). Consequently, the analysis of such data does not provide a direct source of information regarding many-atom interactions. To this category belong third virial coefficients, isotopic separation factors in the liquid, vacancy energies in the solid, etc. Although the analysis of these data appears to indicate that many-atom interactions must be explicitly taken into account for their interpretation, details of the many-atom components are difficult to obtain in this manner. Notable exceptions are data on the stacking-fault energies in the solid and those on crystal stability, where many-atom components of the interaction play a more direct role. For the following analysis we will, consequently, limit ourselves to crystal stability and stacking-fault energies.

The analysis of crystal stability which we have previously given was based on a cluster expansion for the crystal energy of which, besides the pair interactions, only three-particle components were considered. Although it may be expected that physical significance is attached primarily to the three-particle term, the convergence properties of the series should be investigated. Following our formalism, Margenau and Stamper[22] have undertaken a preliminary analysis of four-atom exchange interactions for certain isolated configurations of four rare-gas atoms in the solid, in first-order perturbation theory. They find that for a tetrahedral configuration of nearest-neighbor Ar and Xe atoms the four-atom energy amounts to 17% of the total triplet interaction and that it is of opposite sign. For a square configuration, on the other hand, first-order four-atom interactions are of the same magnitude as the triplet energy, and again of opposite sign.

In this paper, we present an analysis of three- and four-atom exchange interactions in first and second orders of perturbation theory, on the basis of an effective-electron approximation with a Gaussian distribution of charge. On the same basis, we will estimate the stacking-fault energy in solid Ar and Xe.

II. FORMALISM

We consider an arbitrary configuration of three rare-gas atoms (*abc*) or of four such atoms (*abcd*); each atom is characterized by an effective-electron charge density $\rho(r)$ of Gaussian form,

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

where r is the distance from the effective electron to its nucleus and where β is a characteristic parameter, different for different rare-gas atoms. Values of the parameter β for rare-gas atoms are determined in such a way that they fit the long-range (van der Waals) part of a pair potential; typical values are 0.623 Å^{-1} for Ar and 0.454 Å^{-1} for Xe. The ground-state wave function $\phi(r)$ for each isolated atom is the positive square root of Eq. (1). A perturbation calculation including exchange is then carried out to determine the interactions between the atoms in first and second orders; the zeroth-order wave function is a Slater determinant, i.e., for a configuration (*abc*) of three atoms

$$\Psi_0(abc)=[3!(1-\Delta_{abc}{}^2)]^{-1/2}\det\{\phi_a(1)\phi_b(2)\phi_c(3)\}\,, \tag{2}$$

where 1, 2, and 3 denote the effective electrons and where $\Delta_{abc}{}^2$ is expressed in terms of the overlap integrals Δ_{ab}, etc., for the different pairs of atoms. In the case of a four-atom configuration (*abcd*) we have, correspondingly,

$$\Psi_0(abcd)=[4!(1-\Delta_{abcd}{}^2)]^{-1/2}\times\det\{\phi_a(1)\phi_b(2)\phi_c(3)\phi_d(4)\}\,, \tag{3}$$

with $\Delta_{abcd}{}^2$ again expressed in terms of overlap integrals for different pairs. The perturbations H_{abc}', H_{abcd}' and the unperturbed Hamiltonians $H_{abc}{}^{(0)}$, $H_{abcd}{}^{(0)}$ can be written as an additive sum over pair contributions; their operations on symmetrized functions are defined elsewhere.[23]

The formal expressions for the first- and second-order energies of interaction have been given previously[1]; their derivation in case of exchange interactions is presented in detail in Ref. 23. To evaluate the second-order energy, use is made of the Unsöld averaging procedure; then the second-order energy contains the expectation value of the square of the perturbation Hamiltonian H_{abc}' or H_{abcd}'. The zero-order wave functions are those of (2) and (3), respectively.

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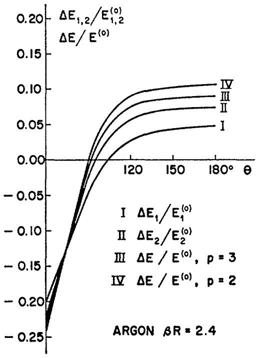

FIG. 1. Relative first-order three-atom energy $\Delta E_1/E_1^{(0)}$, second-order three-atom energy $\Delta E_2/E_2^{(0)}$, and total relative three-atom energy $\Delta E/E^{(0)}$ for isosceles triangles of Ar atoms formed by a central atom and two nearest-neighbors ($\beta R=2.4$), as a function of the opening θ at the central atom. For curves III and IV, the values of $p=|E_2^{(0)}/E_1^{(0)}|$ are 3 and 2, respectively.

Since the unperturbed wave functions are of Gaussian form, all occurring many-center integrals can be readily evaluated, following methods developed recently by Zimering[24] and by Roberts.[25] In either order, the analytical expression for the interaction energy is a sum of contributions depending upon the distances between two atoms, and between three atoms simultaneously, whereas for any configuration of four atoms an additional term appears, involving simultaneously the coordinates of all four atoms. These different terms define what we mean by two-, three-, and four-atom components, respectively, of the perturbation energy.

Given any triplet (*abc*) or quadruplet (*abcd*) of atoms; we denote the *sum* of pair interactions by $E_1^{(0)}$ in first order and by $E_2^{(0)}$ in second order, the three-atom component by ΔE_1 and ΔE_2, respectively, and the four-atom interaction term by $\Delta_4 E_1$ and $\Delta_4 E_2$. Of direct interest are the *relative* many-atom energies $\Delta E_1/E_1^{(0)}$, $\Delta E_2/E_2^{(0)}$ (three-atom relative to pair interactions) and $\Delta_4 E_1/E_1^{(0)}$, $\Delta_4 E_2/E_2^{(0)}$ (four-atom relative to pair interactions). Because these ratios are found to be small compared with unity for any triplet or quadruplet, we may in the second-order expressions $\Delta E_2/E_2^{(0)}$ and $\Delta_4 E_2/E_2^{(0)}$ cancel the Unsöld average energies in numerator and denominator, to a good approximation. This has the advantage that the Unsöld energies need not be known or estimated.

The reasons for determining relative, instead of absolute, many-atom energies are, firstly, because the relative quantities are found to vary in a simple way with the geometry of the configurations considered; secondly, relative quantities are less dependent upon the details of the approximations used. In particular, we have found that different types of perturbation expansion for exchange interactions yield approximately the same results for relative many-atom energies; these results will be published separately.

Explicit expressions for the three-atom first- and second-order energies for an arbitrary triplet (*abc*) have been given previously[1]; they are not reproduced here. The analytical expressions for the first- and second-order *four-atom* interactions for an arbitrary quadruplet (*abcd*) are of enormous complexity, although their derivation is straightforward and no new types of many-center integrals occur beyond those encountered for the three-atom energies. It is not feasible to write these terms in explicit form in the context of the present paper (the first-order expressions are reproduced explicitly by Margenau and Stamper[22]). All terms are linear combinations of seven types of basic integrals listed by Zimering[24]; we refer to this article for further details.

We now describe the method used for evaluating the three- and four-atom components of the crystal energy for rare-gas atoms in the (fcc) and (hcp) configurations. First, for the three-atom energy, we select any triplet (*abc*) and write the total (first- plus second-order) three-atom energy ΔE as $\Delta E=\Delta E_1+\Delta E_2$, or, relative to the total pair energy, $E^{(0)}=E_1^{(0)}+E_2^{(0)}$,

$$\frac{\Delta E}{E^{(0)}}=\frac{\Delta E_1}{E_1^{(0)}}\,\frac{E_1^{(0)}}{E_1^{(0)}+E_2^{(0)}}+\frac{\Delta E_2}{E_2^{(0)}}\,\frac{E_2^{(0)}}{E_1^{(6)}+E_2^{(0)}}.$$

Let us write $E_2^{(0)}/(E_1^{(0)}+E_2^{(0)})=-p$, where $p>1$; otherwise rare-gas crystals would not exist. Substitution yields

$$\frac{\Delta E}{E^{(0)}}=\frac{\Delta E_1}{E_1^{(0)}}+\frac{p}{p-1}\left[\frac{\Delta E_2}{E_2^{(0)}}-\frac{\Delta E_1}{E_1^{(0)}}\right]$$
$$=\frac{\Delta E_2}{E_2^{(0)}}+\frac{1}{p-1}\left[\frac{\Delta E_2}{E_2^{(0)}}-\frac{\Delta E_1}{E_1^{(0)}}\right]. \qquad (4)$$

Except for the quantity $p=|E_2^{(0)}/E_1^{(0)}|$, the relative total three-atom interaction $\Delta E/E^{(0)}$ is herewith expressed in terms of the relative first- and second-order three-atom quantities $\Delta E_1/E_1^{(0)}$ and $\Delta E_2/E_2^{(0)}$, for an arbitrary triplet of rare-gas atoms. It follows from (4) that if $\Delta E_2/E_2^{(0)}>\Delta E_1/E_1^{(0)}$, the value of $\Delta E/E^{(0)}$ is larger than $\Delta E_2/E_2^{(0)}$; if $\Delta E_2/E_2^{(0)}<\Delta E_1/E_1^{(0)}$, then the value for $\Delta E/E^{(0)}$ is smaller than $\Delta E_2/E_2^{(0)}$. With increasing p, on the other hand, $\Delta E/E^{(0)}$ approaches $\Delta E_2/E_2^{(0)}$.

An accurate determination of the values of p for different rare-gas crystals cannot be made. If $E_2^{(0)}$ can be identified with the attractive part of an empirical pair potential, $E_1^{(0)}$ with its repulsive part, then

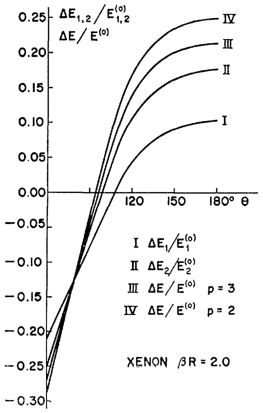

FIG. 2. Relative first-order three-atom energy $\Delta E_1/E_1^{(0)}$, second-order three-atom energy $\Delta E_2/E_2^{(0)}$, and total relative three-atom energy $\Delta E/E^{(0)}$ for isosceles triangles of Xe atoms formed by a central atom and two nearest-neighbors ($\beta R=2.0$), as a function of the opening θ at the central atom. For curves III and IV the values of $p=|E_2^{(0)}/E_1^{(0)}|$ are 3 and 2, respectively.

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TABLE I. Relative first- and second-order four-atom energies $\Delta_4E_1/E_1^{(0)}$ and $\Delta_4E_2/E_2^{(0)}$, as a function of βR, for a tetrahedral and a square configuration. Also given are the ratios $\Delta_4E_1/\Delta E_1$ and $\Delta_4E_2/\Delta E_2$ of the four-atom energies relative to the total three-atom energies. Values in parentheses are the first-order ratios as determined by Margenau and Stamper (Ref. 22).

	Tetrahedron				Square			
βR	$\Delta_4E_1/E_1^{(0)}$	$\Delta_4E_2/E_2^{(0)}$	$\Delta_4E_1/\Delta E_1$	$\Delta_4E_2/\Delta E_2$	$\Delta_4E_1/E_0^{(0)}$	$\Delta_4E_2/E_2^{(0)}$	$\Delta_4E_1/\Delta E_1$	$\Delta_4E_2/\Delta E_2$
1.0	0.0716	0.1093	−0.234	−0.197	0.2732	0.5287	−1.004	−1.221
1.5	0.0847	0.1088	−0.210	−0.195	0.2674	0.3812	−1.068	−1.364
2.0	0.0744	0.0836	−0.176 (−0.176)	−0.167	0.1771	0.1992	−1.135 (−1.198)	−1.740
2.4	0.0564	0.0591	−0.138 (−0.138)	−0.133	0.1058	0.1050	−1.132 (−0.944)	−2.430
3.0	0.0332	0.1473	−0.077	−0.076	0.0495	0.6567	−0.942	−22.960

$E_2^{(0)}/E_1^{(0)}=-\frac{1}{6}s$ for a Lennard-Jones $(6,s)$ potential at nearest-neighbor distance in the solid. In particular, for $s=12$ we would conclude that $p=2$, but this value serves only as a first estimate. In Figs. 1 and 2 we present the results for $\Delta E_1/E_1^{(0)}$, $\Delta E_2/E_2^{(0)}$, and $\Delta E/E^{(0)}$ for isosceles triangles of Ar and Xe atoms in the solid, as a function of the opening angle θ at the central atom. The two remaining atoms of the triplet are at nearest-neighbor distance R from the central atom. The values of the dimensionless parameter βR are 2.4 (solid Ar) and 2.0 (solid Xe). In both cases, $\Delta E/E^{(0)}$ is calculated for $p=|E_2^{(0)}/E_1^{(0)}|=2$ and 3 to illustrate its behavior as a function of p. The values for the relative first- and second-order three-atom energies were obtained using the methods of Zimering and Roberts for the evaluation of the three-center integrals, whereas previously[1] asymptotic series expansions were employed. Qualitatively, the results are quite similar; in particular, as shown in Ref. 1, a θ dependence as exhibited by $\Delta E/E^{(0)}$ favors the fcc configuration for rare-gas crystals.

We follow a similar procedure for the first- and second-order four-atom interactions. For an arbitrary quadruplet, the total (first- plus second-order) four-atom energy Δ_4E can be written as

$$\frac{\Delta_4E}{E^{(0)}}=\frac{\Delta_4E_1}{E_1^{(0)}}\frac{E_1^{(0)}}{E_1^{(0)}+E_2^{(0)}}+\frac{\Delta_4E_2}{E_2^{(0)}}\frac{E_2^{(0)}}{E_1^{(0)}+E_2^{(0)}},$$

where now $E_1^{(0)}$, $E_2^{(0)}$, and $E^{(0)}=E_1^{(0)}+E_2^{(0)}$ are the first-order, second-order, and total pair energies, respectively, summed over all pairs forming the quadruplet considered. The next step consists of introducing a ratio $p'=|E_2^{(0)}/E_1^{(0)}|$, after which $\Delta_4E/E^{(0)}$ can be expressed as

$$\begin{aligned}\frac{\Delta_4E}{E^{(0)}}&=\frac{\Delta_4E_1}{E_1^{(0)}}+\frac{p'}{p'-1}\left[\frac{\Delta_4E_2}{E_2^{(0)}}-\frac{\Delta_4E_1}{E_1^{(0)}}\right]\\&=\frac{\Delta_4E_2}{E_2^{(0)}}+\frac{1}{p'-1}\left[\frac{\Delta_4E_2}{E_2^{(0)}}-\frac{\Delta_4E_1}{E_1^{(0)}}\right],\end{aligned}\tag{5}$$

in complete analogy with the corresponding Eq. (4) for the relative three-atom energy $\Delta E/E^{(0)}$.

To illustrate some general characteristics of four-atom interactions, we consider first the results for a tetrahedral and a square arrangement of atoms; this allows a comparison with the first-order results of Margenau and Stamper.[22] In Table I the relative first- and second-order four-atom energies $\Delta_4E_1/E_1^{(0)}$ and $\Delta_4E_2/E_2^{(0)}$ are given as a function of the dimensionless parameter βR. To compare these results with the corresponding three-atom energies, we also list the ratios $\Delta_4E_1/\Delta E_1$ and $\Delta_4E_2/\Delta E_2$ between the four-atom and the total three-atom energies of the four triangles which form the tetrahedron and the square, respectively. For comparison with the results obtained by Margenau and Stamper, their first-order results for $\Delta_4E_1/\Delta E_1$ are given in parentheses in the table. It is seen that the agreement is excellent for a tetrahedral configuration; the differences for a square arrangement are due to the fact that Margenau and Stamper interpolated graphically from the curves of Ref. 1, which is not as accurate as a direct calculation carried out in the present analysis.

It is interesting to note that for a tetrahedral arrangement the relative first- and second-order four-atom energies are very nearly the same; the four-atom interactions are of opposite sign with respect to three-atom forces, i.e., they produce a quenching of the many-atom energy. Their magnitude relative to the three-atom interactions varies between 8 and 20% for βR between 3 and 1. For a square configuration, on the other hand, the four-atom interactions are of the same order of magnitude as those between three atoms and, again, they are of opposite sign. It should be noted, however, that ΔE_1 and ΔE_2 themselves are much smaller for a square configuration then for a tetrahedron, because of the different geometry of the triplets involved.

III. MANY-ATOM CRYSTAL ENERGY; NUMERICAL RESULTS

We now present the numerical results for first- and second-order four-atom interactions in solid Xe ($\beta R=2.0$) and solid Ar ($\beta R=2.4$). The quadruplet configurations considered are those formed by a central atom and three nearest or next-nearest neighbors, in a fcc and a hcp arrangement. Because the number of atoms in the first shell is 12, in the second shell 6, there are in total 816 of such four-atom arrangements; taking redundant quadruplets into account, this number reduces to 681 quadruplets per atom in the solid. To list

TABLE II. Number of quadrangles, per atom, for the hexagonal and cubic close-packed structures of rare-gas atoms. Each configuration (*abcd*) is defined by the squares of the six distances *ab*, *ac*, *ad*, *bc*, *bd*, and *cd*. The nearest-neighbor distance is taken as unity and *a* is the reference atom.

$(bc)^2$	$(bd)^2$	$(cd)^2$	quad./atom Hex.	quad./atom Cub.	$(bc)^2$	$(bd)^2$	$(cd)^2$	quad./atom Hex.	quad./atom Cub.
$(ab)^2=(ac)^2=(ad)^2=1$									
1	1	1	2	2	1	3	11/3	12	
1	1	2	12	12	1	3	4	24	48
1	1	8/3	3		2	4	2	6	12
1	1	3	9	12	1	11/3	11/3	6	
1	3	2	36	48	2	3	3	12	24
1	2	11/3	12		2	3	11/3	12	
2	2	8/3	6		3	3	8/3	6	
1	3	3	18	24	3	3	3	2	8
1	8/3	11/3	12						
2	1	1	3	3	1	11/3	17/3	24	
2	1	11/3	6		3	3	11/3	12	
3	3	1	36	48	4	3	3	6	12
8/3	1	11/3	12		1	5	5	6	24
1	3	11/3	12		2	3	17/3	12	
2	5	1	6	12	11/3	3	11/3	24	
1	8/3	8/3	18		1	5	17/3	12	
2	3	3	12	24	3	3	5	12	48
1	3	5	48	96	8/3	3	17/3	6	
3	1	17/3	12		3	5	11/3	12	
4	1	5	12	24	2	5	5		12
$(ab)^2=1$ $(ac)^2=(ad)^2=2$									
1	11/3	8/3	12		1	17/3	19/3	24	
1	3	4	24	48	5	5	8/3	6	
3	3	8/3	6		3	11/3	19/3	12	
1	5	4	12	24	11/3	17/3	4	12	
1	3	19/3	12		3	5	19/3	12	
1	11/3	19/3	12		3	5	4		48
3	17/3	8/3	6		1	5	8		24
1	5	19/3	12		3	3	8		24
11/3	11/3	4	6						
$(ab)^2=(ac)^2=(ad)^2=2$									
4	4	4	2	8	4	19/3	19/3	6	
4	8/3	19/3	12		4	4	8		12

these different configurations, we denote the central atom by *a*, the remaining three by *b*, *c*, and *d*, and the sides of the quadrangle by *ab*, *ac*, etc. The configurations can be grouped together according to the different values for the lengths of the sides; all lengths are measured in units of the nearest-neighbor distance R. In this way, four groups appear: for the first group $(ab)^2=(ac)^2=(ad)^2=1$; for the second $(ab)^2=(ac)^2=1$, $(ad)^2=2$ (one of the four atoms in the second shell of neighbors); for the third group $(ab)^2=1$, $(ac)^2=(ad)^2=2$ (two atoms in the second shell), whereas for the last group $(ab)^2=(ac)^2=(ad)^2=2$ (the three atoms are all second neighbors of the central one). In Table II we list, for each group, the lengths of the remaining sides $(bc)^2$, $(bd)^2$, and $(cd)^2$ and the number, per atom, of such configurations in the hexagonal and the cubic structures.

From Eq. (5), the total four-atom energy is computed by summing over all the 681 quadruplets in the two crystal structures, hcp and fcc, as a function of the ratio p' between the total second- and first-order pari interactions for each quadruplet. In a similar manner, the total three-atom energy is determined from (4), as a function of the corresponding ratio p, summed over all the 50 nonredundant triplets per atom, formed by a central atom in either structure and any two of its 12 nearest neighbors. In performing these sums, we consider, in first approximation, only pair interactions between nearest neighbors of the quadruplet or triplet. The total pair interaction between nearest neighbors in the solid is approximately equal to $-\epsilon$, the depth of the pair-potential well. Then $E^{(0)}$ for a four-atom configuration is just a multiple of $-\epsilon$, where the coefficient can be determined directly from Table II, whereas for each triplet $E^{(0)}=-3\epsilon$ for an equilateral triangle and -2ϵ otherwise. In this approximation $p'=p$ for all configurations, the parameter denoting just the absolute ratio of second-order over first-order interactions for a pair of nearest neighbors in the solid. The influence of further neighbors of a central atom can also be taken into account, leading to values of p' and p which are different for different configurations. We have used different values for the ratio of second- to first-order pair interactions for first and second neighbors in the solid; however, the effect on the many-atom crystal energy was found to be negligible.

TABLE III. Total three- and four-atom energies Δ_3 and Δ_4 per atom, in the hcp and fcc configurations for solid Xe ($\beta R=2.0$) as a function of $p(=p')$. The values Δ_3, Δ_4, and $\Delta_3+\Delta_4$ are relative to the total pair energy per atom, which for a Lennard-Jones (6,12) potential is equal to -8.4ϵ, where $-\epsilon$ is the depth of the potential well. The variable parameter $p(=p')$ measures the absolute ratio $|E_2^{(0)}/E_1^{(0)}|$ for a pair of nearest neighbors in the solid.

	Hexagonal			Cubic		
$p(=p')$	Δ_3	Δ_4	$\Delta_3+\Delta_4$	Δ_3	Δ_4	$\Delta_3+\Delta_4$
1.8	0.506	−0.264	0.242	0.512	−0.166	0.346
1.9	0.449	−0.189	0.260	0.454	−0.091	0.363
2.0	0.402	−0.129	0.273	0.407	−0.031	0.376
2.1	0.365	−0.080	0.285	0.369	0.018	0.387
2.2	0.333	−0.039	0.294	0.338	0.059	0.397
2.3	0.307	−0.005	0.302	0.311	0.093	0.404
2.4	0.284	0.025	0.309	0.288	0.122	0.410

In Tables III and IV the results for the total three- and four-atom energies Δ_3 and Δ_4, per atom, in the hcp and the fcc configurations are given for solid Xe ($\beta R=2.0$) and solid Ar ($\beta R=2.4$), relative to the total pair energy, per atom, of the crystal. If we adopt a Lennard-Jones (6,12) potential then this quantity is equal to $-8.4\ \epsilon$ per atom, where $-\epsilon$ is the depth of the pair-potential well. The variable parameter is $p(=p')$, measuring the absolute ratio $|E_2^{(0)}/E_1^{(0)}|$ for a pair of nearest neighbors in the solid. For solid Xe, we select a range of values for p between 1.8 and 2.4 as being most probable; for solid Ar, the results appear to be quite similar to those for solid Xe if the range of p values is chosen between 1.4 and 1.7.

TABLE IV. Total three- and four-atom energies Δ_3 and Δ_4 per atom, in the hcp and fcc configurations for solid Ar ($\beta R=2.4$) as a function of $p(=p')$. The values Δ_3, Δ_4, and $\Delta_3+\Delta_4$ are relative to the total pair energy per atom, which for a Lennard-Jones (6,12) potential is equal to -8.4ϵ, where $-\epsilon$ is the depth of the potential well. The variable parameter $p(=p')$ measures the absolute ratio $|E_2^{(0)}/E_1^{(0)}|$ for a pair of nearest neighbors in the solid.

	Hexagonal			Cubic		
$p(=p')$	Δ_3	Δ_4	$\Delta_3+\Delta_4$	Δ_3	Δ_4	$\Delta_3+\Delta_4$
1.4	0.354	−0.135	0.219	0.358	−0.134	0.224
1.5	0.231	−0.032	0.199	0.235	−0.027	0.208
1.6	0.149	0.036	0.185	0.153	0.045	0.198
1.7	0.091	0.085	0.176	0.095	0.095	0.190

From Table III we note, first of all, that the three-atom crystal energy for solid Xe is attractive over the whole range of p values, whereas the four-atom component is relatively small in either structure for p values in the interval between 1.9 and 2.3. A change of sign, from attractive to repulsive, of the three-atom crystal energy for solid Xe occurs for a value of p larger than approximately 50, but such high values are unrealistic. This change of sign does not affect the stability of the fcc configuration, which is always (with varying p) favored over the hcp structure by very nearly the same percentage of the crystal pair energy. Further, the sum of three- and four-atom energies changes very little when p is varied. It therefore appears justified to conclude that the convergence properties of the cluster expansion for the crystal energy are satisfactory. Furthermore, we conclude, at least in a qualitative sense, that the stability of the fcc configuration is enhanced by considering four-atom interactions in addition to the three-atom component of the crystal energy. It is certain, on the basis of the results of Table III, that four-atom interactions do not reverse conclusions regarding crystal stability obtained on the basis of the three-atom crystal energy alone.

For solid Ar (Table IV) the results are similar to those for solid Xe if the range of p values is chosen between 1.4 and 1.7. The sum of the relative Δ_3 and Δ_4 components is here always smaller than the corresponding values for Xe. Again, both Δ_3 and Δ_4 favor the fcc configuration.

When the range of p values for Ar is extended beyond 1.7, it is found that the three-atom crystal energy goes to zero at p between 1.9 and 2.0, becoming progressively more repulsive at higher values. At $p=3.0$, for example, the repulsion is about 13% of the crystal pair energy. At the same time, the four-atom component, which is already attractive at $p=1.6$, becomes progressively more attractive at higher values of p. The sum of the three- and four-atom contributions, however, varies very little (amounting to 22% for $p=1.4$ and to 15% for $p=3.0$). Over the whole range of p values between 1.4 and 3.0, both the three- and the four-atom components favor the fcc structure, the differences between the two crystal structures remaining practically constant.

On the basis of the present model, some conclusions can also be drawn with regard to the stacking-fault energy in rare-gas crystals. Bullough, Glyde, and Venables[12] have recently estimated the stacking-fault energy in solid Xe and Ar from electron micrographs and associated diffraction patterns of films of these substances grown on a carbon substrate. By comparing the data with those obtained for silver metal, they conclude that the stacking-fault energy in solid Xe is $\leqslant 1.0$ erg/cm^2 and in solid Ar $\leqslant 0.7$ erg/cm^2. Limiting ourselves for the many-atom crystal energy to the nearest neighbors of a central atom, the stacking-fault energy γ (being the energy difference, per unit area of stacking fault, between the crystal with hexagonal fault and the ideal cubic crystal) is given[11] by $\gamma=2(4/a^2 3^{1/2}) \times\delta(E_{\text{hcp}}-E_{\text{fcc}})$, where a is the lattice constant, and $\delta(E_{\text{hcp}}-E_{\text{fcc}})$ is the difference in many-atom crystal energy between the hexagonal and the cubic close-packed structures. The results for Δ_3 and Δ_4 in Tables III and IV can be used directly to calculate the three-atom stacking-fault energy; we will here restrict ourselves to the three-atom contribution. For an average difference in Δ_3 values (over the range of p values considered) of 0.45% for solid Xe and 0.40% for solid Ar, we find $\gamma=1.0$ erg/cm^2 for Xe and $\gamma=0.9$ erg/cm^2 for Ar, in reasonable agreement with the upper limits given by Bullough *et al.*[12] However, it should be remembered that the estimates of the stacking-fault energy are obtained from thin films of molecular crystals; it is not obvious that accurate information can be obtained in this manner.

IV. CONCLUDING REMARKS

In this paper we have presented an analysis of three- and four-atom interactions of exchange type on the basis of a Gaussian effective-electron model. It was found that both the three- and four-atom components of the crystal energy for rare-gas solids favor the fcc configuration, that the sum effect of the many-atom components is attractive in either structure, and that this sum changes little with varying values for the ratio p between second- and first-order interactions for nearest neighbors in the solids. It has also been found that, both for solid Xe and for solid Ar, one can select a range of p values where the four-atom component of the crystal energy is practically negligible with respect to the three-atom energy.

More detailed conclusions regarding these many-atom forces are beyond the scope of the present analysis. It may well be that mainly *mathematical* significance can be attached to the results on the four-atom components, i.e., that these results are mainly of importance in establishing convergence properties for the cluster expansion of the energy for molecular crystals. Furthermore, since accurate theoretical knowledge of the "true" pair potential between rare-gas atoms is lacking, we cannot accurately determine the values of the parameter p.

The difference in many-atom energy between the fcc and hcp structures is found to be practically constant with varying values of p, and it is always in favor of the cubic configuration, in agreement with experiments for solid neon, argon, krypton, and xenon. On the basis of pair interactions only, it is well known[1] that most classes of functions [e.g., the Lennard-Jones (s,6) potentials] favor the hexagonal structure very slightly, namely, to a few hundredths of 1% of the pair energy. The sign of this difference for solid Ar can be reversed, as Alder and Paulson[26] have shown, by an appropriate modification of the pair potential, without drastic influence on the

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[26] B. J. Alder and R. H. Paulson, J. Chem. Phys. **43**, 4172 (1965).

second virial coefficient of the gas. A difference of this order of magnitude can, however, not play a rôle in the problem of crystal stability. The three-atom difference in crystal energy is one order of magnitude larger than that obtained on the basis of pair potentials.

We have undertaken the present analysis principally with the aim of verifying that the Gaussian effective-electron model does not lead to divergent results in passing from clusters of three atoms to four-atom configurations. In view of the large values of nearest-neighbor overlap integrals for the heavy rare-gas solids obtained with the Gaussian effective orbitals, such a verification is important within the framework of the model itself. The large overlap results from the manner in which the Gaussian parameter β is determined, namely, adapted to the long- and the short-range components of the pair potentials between near atoms and then extrapolated to the heavier rare-gas atoms. The postulatory basis for this procedure is the assumption that *relative* many-atom interactions can reliably be calculated in this way. Recent criticisms of the Gaussian effective-electron approach, in particular those formulated by Swenberg,[27] must be viewed in this light.[28]

We have also found that, for *isolated* quadruplets of atoms, the four-atom interactions may in some cases (e.g., a square configuration) be of the same magnitude as the three-atom energy. Finally, the results of this analysis as applied to the stacking-fault energy in solid Ar and solid Xe seem to be in reasonable agreement with estimates obtained from observations on thin films of these crystals.[12] Definite conclusions must here await the development of more accurate methods for measuring the stacking-fault energy.

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Radiation Damage in ZnO Single Crystals*

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The radiation and additive coloration of Li-doped and "pure" ZnO crystals have been investigated. The radiation coloration is enhanced by the presence of Li impurity when the radiation temperature is in the range 80–330°K, but the additive coloration is suppressed in Li-doped specimens. The defect production rate, as measured by the increased optical absorption of the samples, is a linear function of electron irradiation intensity and decreases with irradiation energy. The energy dependence of the electron coloration suggests that the defect giving rise to the coloration is produced by the displacement of zinc ions. For a given dose of radiation, fast neutrons (>1 MeV) produce about 30 times as many defects as do energetic electrons. In irradiated crystals the coloration anneals out around 250°C, whereas in additive colored samples the annealing-out temperature is about 900°C. γ irradiation during and after annealing indicates that in both cases annealing is complete and not due only to the loss of electrons or holes from the defect center. It is concluded from the study that radiation damage in ZnO occurs primarily as a result of elastic collisions, and that the photochemical processes prevalent in alkali halides contribute very little, if any, to the damage.

INTRODUCTION

THE electrical and optical properties of zinc oxide have been the subject of a number of investigations during the last two decades, and a comprehensive review of these studies up to the year 1958 has been presented by Heiland, Mollwo, and Stöckmann.[1] A more recent survey by Kroger[2] gives a complete list of references as well as a discussion of defect models. The primary obstacle to understanding the effect of defects on the optical and electrical properties of this material appears to be that until recently only a few measurements had been made on single crystals; therefore, since these properties vary greatly when the chemical and mechanical purity of specimens is not high, it is difficult to make a consistent interpretation of all the available results. Our work involves the use of ZnO single crystals and so we will emphasize the experiments done on single

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