than in the case of $CuCl_2 \cdot 2H_2O$, but still not large in comparison to the exchange energy. Thus, Date's theory offers no special advantage over the Nagamiya-Yosida theory for $MnCl_2 \cdot 4H_2O$. Both theories, however, are deficient, since microwave resonances occur at magnetic-field values which are comparable to the low exchange field in $MnCl_2 \cdot 4H_2O$ ($\sim 12\,000$ Oe at $1°K$). The only theory which is valid for large external fields is that of Gorter and Haantjes,[16] but its applicability is limited to the case of $T = 0°K$. Thus, there exists no theory at present which is suitable for all of our experimental observations in $MnCl_2 \cdot 4H_2O$.

The expectation that the Nagamiya-Yosida theory should be approximately valid in $MnCl_2 \cdot 4H_2O$ for low-field resonances and should become increasingly poor at higher values of the external field was borne out.

An unexpected deviation from the theory in a region where it should be valid, however, occurred at very low temperatures. A low-field b-axis resonance, which conformed very well to the theory in the temperature region of 0.6 to $1.6°K$ began to exhibit a marked deviation from the theory below $0.6°K$. In addition a new resonance appeared in this low-temperature region which exhibited properties similar to the critical-field resonance as regards linewidth, temperature dependence, and resonance behavior upon rotation of H_0 into the ac and bc planes. We do not have an explanation of these deviations but the possibility of a change in magnetic structure such as the formation of additional sublattices ought not to be excluded. Low-temperature neutron diffraction studies would be highly desirable to complement this study.

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

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By extending the theory developed in a previous publication for the stability of rare-gas crystals, it is shown that the stability of alkali-halide crystals can be explained in terms of three-body exchange interactions between the ions. As in the case of rare-gas crystals, the analysis is based on a first- and second-order perturbation calculation with a Gaussian effective-electron model. The different size of anion and cation of each solid is taken into account. The effect on stability of double-exchange contributions to the three-body energy (negligible for rare-gas crystals) is analyzed in detail. It is shown that the theory accounts for all observed regularities on a quantitative basis. In particular, cesium chloride, bromide, and iodide are found to be stable in the cesium chloride modification; furthermore, calculated and observed values for the pressure of transition from the sodium chloride to the cesium chloride configuration are in good agreement.

INTRODUCTION

ACCORDING to the Born-Mayer theory of ionic crystals, all alkali halides should crystallize at normal pressures and temperatures in the sodium chloride structure (two interpenetrating face-centered cubic lattices), this configuration being favored over the cesium chloride structure (two interpenetrating simple-cubic lattices) by as much as a few kcal/mole. However, all cesium halides, except its fluoride, show the cesium chloride modification, whereas all rubidium and potassium halides, except potassium fluoride, have been found to exhibit pressure transitions from the sodium chloride to the cesium chloride structure. Such transitions are indeed predicted by the Born-Mayer theory, but the calculated transition pressures for the heavier alkali halides are considerably higher than those observed. For example, rubidium chloride has an experimental transition pressure of 4900 atm, whereas the calculated value is 39 000 atm.

This stability problem has received extensive attention in the literature; for detailed reviews we refer to the excellent treatises by Born and Huang[1] and by Pauling.[2] Historically, the first analysis was carried out by Hund[3] on the basis of a pair potential between the ions consisting of electrostatic interactions between point charges and a repulsive potential varying as the inverse nth power with distance. It was found that the cesium chloride modification is only stable for values of n higher than 30, but such high values are incompatible with experimental results on compressibilities of the

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[1] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Chaps. I and III.
[2] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1948), Chap. X.
[3] F. Hund, Z. Physik 34, 833 (1925).

crystals. Born and Mayer[4] analyzed the stability on the basis of an exponentially decreasing repulsive potential plus electrostatic interactions (Born-Mayer potential); they took into account also attractive second-order (van der Waals) interactions between the ions. The sodium chloride structure was consistently found to be the more stable configuration.

A recalculation of the cesium chloride stability by May[5] on the basis of careful new estimates of van der Waals interactions by Mayer[6] gave essentially the same results. Jacobs[7] then calculated for the different alkali halides the pressures at which a transition should occur from the sodium chloride to the cesium chloride structure, taking values for the van der Waals interactions as determined by Mayer. The calculated pressures for the heavier halides were considerably higher than those observed.

It appeared, therefore, that in calculating the *difference* between the lattice energies of the sodium chloride and cesium chloride modifications on the basis of a Born-Mayer potential, the energy of the cesium chloride structure is *under*estimated by a few kcal/mole for the heavier alkali halides. This implies that the Born-Mayer potential must be made *structure-dependent*, i.e., with different parameters for different crystal structures, in order to explain the data. It is obvious that the Born-Mayer potential is in principle different for different structures since it represents a weighted average of interactions between a central ion and its first few shells of neighbors. However, in view of the short-range character of repulsive forces, such effects cannot lead to an energy difference as high as a few kcal/mole between the cesium chloride and the sodium chloride modifications.

In a recent phenomenological analysis of transition data for the alkali halides Tosi and Fumi[8] have shown that a simple, two-term, structure-dependent Born-Mayer potential can indeed account for the work involved in the pressure transitions for the rubidium and potassium halides and for the heat absorbed in the observed temperature transition of cesium chloride.[9] As the only remaining possible explanation for the structure dependence we assume that this effect is induced by *many-body* interactions between the ions. Such interactions must be large, and highly sensitive with respect to crystal structure, i.e., they must be of *short range* (*exchange* type) and of low order of perturbation theory. We will consider three-body interactions only, i.e., simultaneous interactions between *triplets* of ions in the two structures.

The first theoretical analysis of many-body inter-

actions in alkali-halide crystals was undertaken by Löwdin.[10] He found from first-order perturbation theory a considerable many-body component of the interactions, amounting to 10–20 kcal/mole, with negative sign, for alkali halides with small positive and large negative ions. However, this many-body contribution decreases rapidly as the ions approach equal size and its magnitude is practically proportional to the Madelung energy of the crystal. Since the Madelung constants of the cesium chloride and sodium chloride configurations differ by only 1%, the structure sensitivity of this effect is much too small to account for stability. Other attempts have been made to introduce many-body components of the interactions, but these have no direct bearing on stability; they will be mentioned at the end of this paper. We will show how the stability of alkali crystals can be understood in terms of three-body exchange interactions between the ions in first and second orders of perturbation theory. The following analysis bears close resemblance to that given in a previous publication,[11] hereafter referred to as I, for the stability of rare-gas crystals. Preliminary results of the analysis have been reported earlier.[12]

THREE-BODY INTERACTIONS BETWEEN CLOSED-SHELL IONS

In I we have assumed that there exists a close similarity between the stability problems of alkali-halide and rare-gas crystals. This assumption is based on the fact that the alkali-halide ions are isoelectronic with rare-gas atoms and that both consist of closed electron shells. Consequently, their interactions must be of the same form if we subtract purely electrostatic forces between the ion charges and disregard polarization effects in view of the high symmetry of unstrained ionic crystals.

We use, therefore, the same method as in I for the evaluation of three-body interactions, namely, an effective-electron model with one such electron per ion. The charge distribution of the effective electron is chosen to be of Gaussian form,

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

where r is the distance between the effective electron and its nucleus and where β is a characteristic parameter, different for different ions. Since the Gaussian model is used only to evaluate *three-body* interactions (which we assumed to be of the same type as those between rare-gas atoms with respect to their importance for stability), ions and atoms are treated on the same basis. In other words, we assume that, except through the Madelung energy, the net charges of the ions play no essential role for the stability of alkali-halide crystals.

[4] M. Born and J. E. Mayer, Z. Physik **75**, 1 (1932).
[5] A. May, Phys. Rev. **52**, 339 (1937); **54**, 629 (1938).
[6] J. E. Mayer, J. Chem. Phys. **1**, 270 (1933).
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[8] M. P. Tosi and F. G. Fumi, Phys. Chem. Solids **23**, 359 (1962).
[9] At a temperature of 718°K and at normal pressure, cesium chloride goes over from the cesium chloride to the sodium chloride structure.

[10] P. O. Löwdin, *A Theoretical Investigation into Some Properties of Ionic Crystals* (Almqvist and Wiksell boktryckeri AB, Uppsala, 1948); Phil. Mag. Suppl. **5**, 1 (1956).
[11] L. Jansen, Phys. Rev. **135**, A1292 (1964).
[12] L. Jansen and E. Lombardi, Phys. Rev. Letters **12**, 11 (1964).

We continue to use the names ion, cation, and anion, even though in the one-effective-electron model they are charged neutral.

It should also be remarked at the outset that the limitation to one effective electron per ion (atom) implies that we consider only contributions to the three-body energy due to the exchange of *one pair* of electrons between the same pair of ions. This approximation holds for rare-gas crystals. However, the nearest-neighbor distances in alkali-halide crystals are relatively considerably smaller because of strong compression of the lattice due to the Madelung energy. Therefore, the validity of this *single-exchange* approximation must be investigated for alkali-halide crystals. In a later section we will undertake a detailed analysis of double-exchange contributions to the energy as a function of interionic distances and ionic dimensions. In this section we discuss single exchange only.

Consider a triplet (abc) of Gaussian ions with one effective electron per ion, counterbalanced by nuclear charges of plus one. The zero-order wave function is (Slater determinant)

$$\Psi^{(0)} = [3!(1-\Delta^2_{abc})]^{-1/2} \det\{\varphi_a[1]\varphi_b[2]\varphi_c[3]\}, \quad (2)$$

where 1, 2, 3 number the electrons. The wave function for ion a is given by

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

i.e., by the positive square root of the Gaussian density (1). The quantity Δ_{abc} is a total overlap integral, defined by

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

in terms of the overlap integrals Δ_{ab}, etc., between the different pairs of ions. Further, β_a is the Gaussian parameter for ion a. 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.

Each alkali halide can be represented by a pair (β,β') of Gaussian parameters. We adopt the convention $\beta' > \beta$, i.e., β' represents the *smaller* ion and β the *larger* ion. The total three-body energy for a given crystal structure is then obtained by summing three-body interactions over all possible triplets of ions. This total three-body component appears to be completely determined by the parameter $\gamma = (\beta'/\beta)^2 > 1$, by the dimensionless quantity βR, where R is the nearest-neighbor distance in the lattice, and by the crystal symmetry.

First- and Second-Order Three-Body Interactions

For the *first-order* energy E_1 of the triplet (abc), we have to evaluate

$$E_1 = \langle H'_{abc} \rangle = \langle H'_{ab} \rangle + \langle H'_{ac} \rangle + \langle H'_{bc} \rangle,$$

with the zero-order wave function (2); E_1 gives the closed-shell repulsion between the ions. The expressions are very similar to those concerning a triplet of rare gas atoms[13]; the only formal difference being that the ions a, b, c need not be identical. The result for $\langle H'_{ab} \rangle$ is

$$
\begin{aligned}
\langle H'_{ab} \rangle/e^2 \\
= 1/R_{ab} + 1/(1-\Delta^2_{abc})^{-1}\{ -(1-\Delta^2_{bc})G_{aa(b)} \\
- (1-\Delta^2_{ac})G_{bb(a)} + (\Delta_{ab}-\Delta_{ac}\Delta_{bc})[G_{ab(a)}+G_{ab(b)}] \\
+ (\Delta_{ac}-\Delta_{ab}\Delta_{bc})G_{ac(b)} + (\Delta_{bc}-\Delta_{ab}\Delta_{ac})G_{bc(a)} \\
+ (A_{abab}-A_{aabb}) + \Delta_{ac}(A_{abbc}-A_{abcb}) \\
+ \Delta_{bc}(A_{aabc}-A_{abac})\}. \quad (5)
\end{aligned}
$$

Here the symbols G and A are abbreviations for the following integrals:

$$G_{ab(c)} = \int \frac{\varphi_a \varphi_b}{r_c} d\tau, \quad G_{aa(b)} = \int \frac{\varphi_a \varphi_a}{r_b} d\tau,$$

etc., with r_c = distance between an electron and nucleus of ion c, r_b = distance between an electron and nucleus of ion b, and

$$A_{abac} = \int \int \frac{\varphi_a(1)\varphi_b(2)\varphi_a(1)\varphi_c(2)}{r_{12}} d\tau_1 d\tau_2,$$

$$A_{aabc} = \int \int \frac{\varphi_a(1)\varphi_a(2)\varphi_b(1)\varphi_c(2)}{r_{12}} d\tau_1 d\tau_2,$$

etc., with r_{12} = distance between electrons 1 and 2.

Table I contains the integrals occuring in the equation for E_1 and their values for Gaussian charge distributions, for the case $\beta_a = \beta'$, $\beta_b = \beta_c = \beta$. Methods for evaluating these integrals have been developed by Boys,[14] Shavitt,[15] and Zimering.[16]

The quantities which appear in Table I are defined as follows: R_{ab}, R_{ac}, R_{bc} are the lengths of the sides ab, ac, bc; $(_{ab},\gamma)$ is that point on ab, whose distance from a is equal to $(1/\gamma+1)R_{ab}$; (ac,γ) is that point on ac, whose distance from a is equal to $(1/\gamma+1)R_{ac}$; $R_{a(bc)}$ = distance between a and the middle of bc; $R_{c(ab,\gamma)}$ = distance between c and the point (ab,γ), etc., $R_{(ab,\gamma)(ac,\gamma)}$ = distance between the points (ab,γ) and (ac,γ), etc., $R_{(ab,\gamma)(bc)}$ = distance between the point (ab,γ) and the middle of bc.

The integrals of Table I can also be used to calculate, in units of β, the values of the different integrals for the case $\beta_a = \beta$; $\beta_b = \beta_c = \beta'$ provided that the following substitutions are made: (i) γ is replaced by $1/\gamma$; (ii) β is replaced by $\beta\gamma^{1/2}$; (iii) the resulting expression is multiplied by $\gamma^{1/2}$.

[13] L. Jansen, Phys. Rev. 125, 1798 (1962).
[14] S. F. Boys, Proc. Roy. Soc. (London) A200, 542 (1950).
[15] I. Shavitt, *Methods in Computational Analysis* (Academic Press Inc., New York, 1963), Vol. 2, p. 1.
[16] S. Zimering (to be published).

TABLE I. List of integrals for E_1, for the case $\beta_a=\beta'$, $\beta_b=\beta_c=\beta$, in units of β, and their values for Gaussian distributions of charge.

Integral	Value for Gaussian distribution $\langle H'_{ab}\rangle$	Integral	Value for Gaussian distribution $\langle H'_{ab}\rangle$
$\Delta_{ab}{}^{(\gamma)}$	$\left(\dfrac{2\gamma^{1/2}}{\gamma+1}\right)^{3/2}\exp\left[\dfrac{-\gamma\beta^2R^2_{ab}}{2(\gamma+1)}\right]$	$G_{ab(c)}$	$\Delta_{ab}{}^{(\gamma)}\dfrac{1}{\beta R_{c(ab,\gamma)}}\mathrm{erf}\left[\dfrac{(\gamma+1)^{1/2}}{2^{1/2}}\beta R_{c(ab,\gamma)}\right]$
$G_{aa(b)}$	$\dfrac{1}{\beta R_{ab}}\mathrm{erf}(\beta\gamma^{1/2}R_{ab})$	A_{acac}	$\dfrac{1}{\beta R_{ac}}\mathrm{erf}\left[\left(\dfrac{\gamma}{\gamma+1}\right)^{1/2}\beta R_{ac}\right]$
$G_{bb(a)}$	$\dfrac{1}{\beta R_{ab}}\mathrm{erf}(\beta R_{ab})$	A_{aacc}	$\left(\dfrac{\gamma+1}{\pi}\right)^{1/2}\Delta_{ac}{}^{(\gamma)2}$
$G_{ab(a)}$	$\Delta_{ab}{}^{(\gamma)}\dfrac{\gamma+1}{\beta R_{ab}}\mathrm{erf}\left[\dfrac{\beta R_{ab}}{2^{1/2}(\gamma+1)^{1/2}}\right]$	A_{acab}	$=A_{abac}$
$G_{ab(b)}$	$\Delta_{ab}{}^{(\gamma)}\dfrac{\gamma+1}{\beta\gamma R_{ab}}\mathrm{erf}\left[\dfrac{\beta\gamma R_{ab}}{2^{1/2}(\gamma+1)^{1/2}}\right]$	A_{acbc}	$\dfrac{\Delta_{ab}{}^{(\gamma)}}{\beta R_{c(ab,\gamma)}}\mathrm{erf}\left[\left(\dfrac{\gamma+1}{\gamma+3}\right)^{1/2}\beta R_{c(ab,\gamma)}\right]$
$G_{bc(a)}$	$\Delta_{bc}\dfrac{1}{\beta R_{a(bc)}}\mathrm{erf}(\beta R_{a(bc)})$	A_{aacb}	$=A_{aabc}$
$G_{ac(b)}$	$\Delta_{ac}{}^{(\gamma)}\dfrac{1}{\beta R_{b(ac,\gamma)}}\mathrm{erf}\left[\dfrac{(\gamma+1)^{1/2}}{2^{1/2}}\beta R_{b(ac,\gamma)}\right]$	A_{accb}	$\dfrac{\Delta_{ac}{}^{(\gamma)}\Delta_{bc}}{\beta R_{(ac,\gamma)(bc)}}\mathrm{erf}\left[\left(\dfrac{\gamma+1}{\gamma+3}\right)^{1/2}\beta R_{(ac,\gamma)(bc)}\right]$
A_{abab}	$\dfrac{1}{\beta R_{ab}}\mathrm{erf}\left[\left(\dfrac{\gamma}{\gamma+1}\right)^{1/2}\beta R_{ab}\right]$	A_{aaac}	$\dfrac{\Delta_{ac}{}^{(\gamma)}(\gamma+1)}{\beta R_{ac}}\mathrm{erf}\left[\dfrac{\gamma^{1/2}\beta R_{ac}}{(\gamma+1)^{1/2}(3\gamma+1)^{1/2}}\right]$
A_{aabb}	$\left(\dfrac{\gamma+1}{\pi}\right)^{1/2}\Delta_{ab}{}^{(\gamma)2}$	A_{accc}	$\dfrac{\Delta_{ac}{}^{(\gamma)}(\gamma+1)}{\beta R_{ac}}\mathrm{erf}\left[\dfrac{\gamma\beta R_{ac}}{(\gamma+1)^{1/2}(\gamma+3)^{1/2}}\right]$
A_{abac}	$\dfrac{\Delta_{bc}}{\beta R_{a(bc)}}\mathrm{erf}\left[\left(\dfrac{\gamma}{\gamma+1}\right)^{1/2}\beta R_{a(bc)}\right]$	Δ_{bc}	$\exp\left(-\dfrac{\beta^2R^2_{bc}}{4}\right)$
A_{abcb}	$=A_{bcba}$	$G_{bb(c)}$	$\dfrac{1}{\beta R_{bc}}\mathrm{erf}(\beta R_{bc})$
A_{aabc}	$\dfrac{\Delta_{ab}{}^{(\gamma)}\Delta_{ac}{}^{(\gamma)}}{\beta R_{(ab,\gamma)(ac,\gamma)}}\mathrm{erf}\left[\dfrac{(\gamma+1)^{1/2}}{2}\beta R_{(ab,\gamma)(ac,\gamma)}\right]$	$G_{cc(b)}$	$=G_{bb(c)}$
A_{abbc}	$=A_{bbca}$	$G_{bc(b)}$	$\Delta_{bc}\dfrac{2}{\beta R_{bc}}\mathrm{erf}\left(\dfrac{\beta R_{bc}}{2}\right)$
A_{aaab}	$\dfrac{\Delta_{ab}{}^{(\gamma)}(\gamma+1)}{\beta R_{ab}}\mathrm{erf}\left[\dfrac{\gamma^{1/2}\beta R_{ab}}{(\gamma+1)^{1/2}(3\gamma+1)^{1/2}}\right]$	$G_{bc(c)}$	$=G_{bc(b)}$
A_{abbb}	$\dfrac{\Delta_{ab}{}^{(\gamma)}(\gamma+1)}{\gamma\beta R_{ab}}\mathrm{erf}\left[\dfrac{\gamma\beta R_{ab}}{(\gamma+1)^{1/2}(\gamma+3)^{1/2}}\right]$	$G_{ca(b)}$	$=G_{ac(b)}$
$\Delta_{ac}{}^{(\gamma)}$	$\left(\dfrac{2\gamma^{1/2}}{\gamma+1}\right)^{3/2}\exp\left[-\dfrac{\gamma\beta^2R^2_{ac}}{(\gamma+1)}\right]$	$G_{ba(c)}$	$=G_{ab(c)}$
$G_{aa(c)}$	$\dfrac{1}{\beta R_{ac}}\mathrm{erf}(\beta\gamma^{1/2}R_{ac})$	A_{bcbc}	$\dfrac{1}{\beta R_{bc}}\mathrm{erf}\left[\dfrac{\beta R_{bc}}{2^{1/2}}\right]$
$G_{cc(a)}$	$\dfrac{1}{\beta R_{ac}}\mathrm{erf}(\beta R_{ac})$	A_{bbcc}	$\left(\dfrac{2}{\pi}\right)^{1/2}\Delta^2_{bc}$
$G_{ac(a)}$	$\Delta_{ac}{}^{(\gamma)}\dfrac{\gamma+1}{\beta R_{ac}}\mathrm{erf}\left[\dfrac{\beta R_{ac}}{2^{1/2}(\gamma+1)^{1/2}}\right]$	A_{bcba}	$\dfrac{\Delta_{ac}{}^{(\gamma)}}{\beta R_{b(ac,\gamma)}}\mathrm{erf}\left[\left(\dfrac{\gamma+1}{\gamma+3}\right)^{1/2}\beta R_{b(ac,\gamma)}\right]$
$G_{ac(c)}$	$\Delta_{ac}{}^{(\gamma)}\dfrac{\gamma+1}{\beta\gamma R_{ac}}\mathrm{erf}\left[\dfrac{\beta\gamma R_{ac}}{2^{1/2}(\gamma+1)^{1/2}}\right]$	A_{bcac}	$=A_{acbc}$
$G_{cb(a)}$	$=G_{bc(a)}$	A_{bbca}	$\dfrac{\Delta_{ab}{}^{(\gamma)}\Delta_{bc}}{\beta R_{(ab,\gamma)(bc)}}\mathrm{erf}\left[\left(\dfrac{\gamma+1}{\gamma+3}\right)^{1/2}\beta R_{(ab,\gamma)(bc)}\right]$
		A_{bcca}	$=A_{accb}$
		A_{bbbc}	$\dfrac{2\Delta_{bc}}{\beta R_{bc}}\mathrm{erf}\left[\dfrac{\beta R_{bc}}{2^{3/2}}\right]$
		A_{bccc}	$=A_{bbbc}$

It is also easily verified that by putting $\gamma=1$ the integrals are reduced to the same form as that for rare-gas atoms.[13]

The first-order energy between a and b *without c* present, $\langle H'_{ab}\rangle^{(0)}$, is obtained from (5) by removing ion c to infinity. The result is

$$\langle H'_{ab}\rangle^{(0)}/e^2 = \frac{1}{R_{ab}} + \frac{1}{1-\Delta^2_{ab}}\{-G_{aa(b)}-G_{bb(a)}$$

$$+\Delta_{ab}[G_{ab(a)}+G_{ab(b)}]+(A_{abab}-A_{aabb})\}. \quad (6)$$

Again, the corresponding equations for $\langle H'_{ac}\rangle^{(0)}$ and $\langle H'_{bc}\rangle^{(0)}$ are obtained from (6) by obvious substitutions. The *three-body* component of $\langle H'_{ab}\rangle/e^2$, namely,

$$\{\langle H'_{ab}\rangle-\langle H'_{ab}\rangle^{(0)}\}/e^2,$$

is obtained by subtracting (6) from (5). In the same manner we form the total three-body first-order energy for the triplet (abc). Finally, the relative first-order three-body energy, which we denote by $\Delta E_1/E_1^{(0)}$, is given by

$$\Delta E_1/E_1^{(0)} = \{\langle H'_{abc}\rangle-\langle H'_{abc}\rangle^{(0)}\}/\langle H'_{abc}\rangle^{(0)}, \quad (7)$$

where

$$E_1^{(0)} = \langle H'_{abc}\rangle^{(0)} = \langle H'_{ab}\rangle^{(0)}+\langle H'_{ac}\rangle^{(0)}+\langle H'_{bc}\rangle^{(0)}$$

is the sum of first-order pair interactions (6) for the triplet.

The three-body energies for the cesium chloride and sodium chloride configurations are obtained by summing over all triplet interactions in the two structures. In either lattice a central cation is surrounded by a first shell of anions, followed by a second shell of cations; for a central anion the situation is, of course, just the reverse. Since the three-body interactions are of short range, the main contributions arise from triangles of smallest dimensions. We indicate these triangles by the triplet of Gaussian parameters for the ions, where the first parameter represents the central ion. Thus, the smallest triangles are denoted by $(\beta\beta'\beta')$ and $(\beta'\beta\beta)$, followed by $(\beta\beta\beta)$ and $(\beta'\beta'\beta')$. The first two types refer to isosceles triangles formed by a central ion and two of its nearest neighbors; the last two types refer to isosceles triangles formed by a central ion and two of its *next*-nearest neighbors. We note that the contributions from the triangles $(\beta\beta\beta)$ and $(\beta'\beta'\beta')$ to the three-body energy can be evaluated directly as for rare-gas crystals.

The values of the parameter β for rare-gas atoms can be determined from pair potential functions, both at large and at small interatomic distances.[13] From these, the values of βR can be calculated; they lie between 2.0 (solid xenon) and 3.4 (solid neon). For alkali-halide ions we do not know such pair potentials; therefore, β and γ must be determined in a different manner. In a later section, these values will be estimated from diamagnetic susceptibilities of the ions. It is to be noted that the precise values of β and γ are not of direct importance
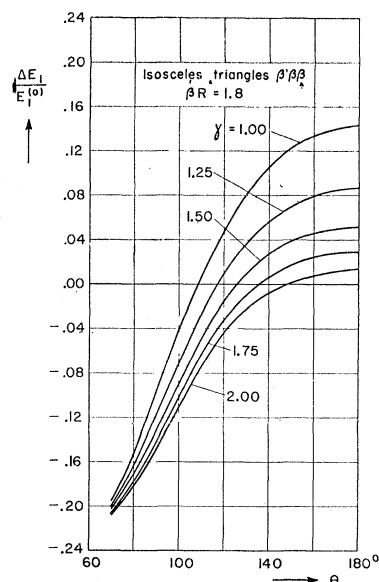

FIG. 1. Relative first-order three-body energy $\Delta E_1/E_1^{(0)}$ as a function of the opening θ of isosceles triangles $(\beta'\beta\beta)$, i.e., those with the *smaller* ion at the center, for $\beta R=1.8$ and $\gamma=(\beta'/\beta)^2=1.00$, 1.25, 1.50, 1.75, and 2.00.

since we are primarily interested in their *range* of values for the alkali halides. For βR this range extends from 1.3 to 2.1 and for γ from 1 to 20 or higher.

For the stability problem we are essentially interested in those alkali halides which exhibit the cesium chloride structure under normal or moderate pressures, i.e., in the cesium and rubidium halides except the fluorides. For these halides βR lies in the neighborhood of 1.8 and γ assumes values between 1 and 2. We will find that in these cases the three-body component of the lattice energy is determined essentially by contributions from the triangles of types $(\beta'\beta\beta)$ and $(\beta\beta'\beta')$, whereas the triplets $(\beta\beta\beta)$ and $(\beta'\beta'\beta')$ are relatively unimportant. On the other hand, the more dissimilar the ions are in size, i.e., the larger the value of γ, the more important contributions from triplets $(\beta\beta\beta)$ of the larger ions to the three-body energy become.

In Figs. 1 and 2 we give the results for the relative first-order three-body energy $\Delta E_1/E_1^{(0)}$ as a function of the opening θ of the isosceles triangles $(\beta'\beta\beta)$ and $(\beta\beta'\beta')$ for $\beta R=1.8$, and $\gamma=1$; 1.25; 1.50; 1.75; and 2.00. The results were obtained from (7), (6), and (5) on an IBM-1620 computer. We draw the following conclusions:

(1) $\Delta E_1/E_1^{(0)}$ as a function of θ *exhibits the same general behavior as for rare-gas crystals*[11]: the relative three-body energy is *negative* for triangles with small opening; increases rapidly with θ until $\theta \sim 120°$ and then flattens off very markedly, assuming positive values for triangles with large opening.

(2) For triangles $(\beta'\beta\beta)$, i.e., those with the *smaller* ion at the center, increasing γ has a negligible effect for small θ, whereas the three-body energy is quenched considerably for large values of θ.

(3) The *opposite* behavior from (2) is exhibited by triangles $(\beta\beta'\beta')$, i.e., those with the *larger* ion at the center.
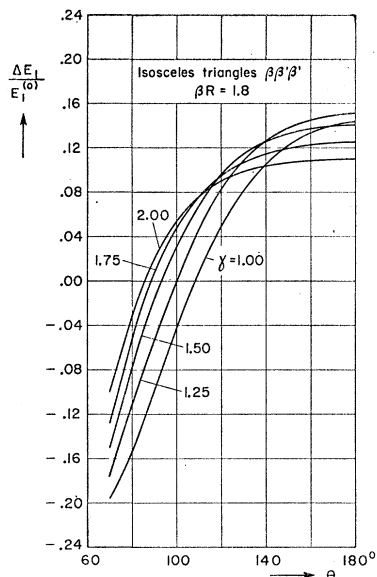
FIG. 2. Relative first-order three-body energy $\Delta E_1/E_1^{(0)}$ as a function of the opening θ of isosceles triangles ($\beta\beta'\beta'$), i.e., those with the *larger* ion at the center for $\beta R=1.8$ and $\gamma=(\beta'/\beta)^2=1.00$, 1.25, 1.50, 1.75, and 2.00.

of ions,

$$E_2=\sum_{\kappa\neq0}\frac{(H'_{abc})_{0\kappa}(H'_{abc})_{\kappa0}}{E_0-E_\kappa}$$

$$=\frac{1}{E_{\mathrm{av}}}\langle[H'_{abc}-\langle H'_{abc}\rangle]^2\rangle, \quad (8)$$

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 (2).

The quantity of direct interest is again the relative three-body energy for the triplet, defined by

$$\Delta E_2/E_2^{(0)}=(E_2-E_2^{(0)})/E_2^{(0)}, \quad (9)$$

where $E_2^{(0)}$ denotes the sum of second-order energies between the three *isolated* pairs of ions which form the triangle. In I, $\Delta E_2/E_2^{(0)}$ was analyzed for rare-gas crystals; detailed numerical results were given for solid argon ($\beta R=2.4$). *It was found that the relative first- and second-order three-body interactions are practically the same at all values of the opening θ of isosceles triangles formed by a central atom and two of its nearest neighbors in the crystal.*

The analysis of second-order three-body interactions between alkali-halide ions can be carried through without detailed calculations in two limiting cases. First, we consider γ values between 1 and 2; $\beta R\sim1.8$. In the present section we found that for such values the first-order energies $\Delta E_1/E_1^{(0)}$ are very similar to those for rare-gas atoms. It must be expected that this similarity extends to second-order interactions. Specifically, we assume that in this range the relation $\Delta E_1/E_1^{(0)}\approx\Delta E_2/E_2^{(0)}$ holds also for three-body interactions between ions. Secondly, for values of $\gamma\gg1$ we found that the

Since $E_1^{(0)}>0$, we conclude that in all cases first-order three-body interactions *favor triangles with small opening* θ, as in the case of rare-gas crystals.

If, on the other hand, the cation is much smaller than the anion, i.e., if $\gamma\gg1$, then we expect more drastic changes in the behavior of $\Delta E_1/E_1^{(0)}$. This is shown in Figs. 3 and 4, where $\Delta E_1/E_1^{(0)}$ is given for triplets ($\beta'\beta\beta$) and ($\beta\beta'\beta'$) as a function of θ, for $\beta R=1.5$ and $\gamma=2$; 4; 10; 20 and an extreme value $\gamma=100$. For comparison, the values for $\gamma=1$ are also reported. From Fig. 3 and 4 we draw the following conclusions:

(1') In the case of triplets ($\beta'\beta\beta$) we see (Fig. 3) that $\Delta E_1/E_1^{(0)}$ becomes practically independent of γ for $\theta>150°$, whereas the values for small θ increase rapidly with γ.

(2') In the case of triplets ($\beta\beta'\beta'$), with a much larger ion at the center, we see (Fig. 4) that the three-body interactions are independent of θ for $\gamma\geq10$. For $\gamma\sim4$ the values increase very sharply for the smallest openings and then remain practically constant.

Generally, we see that with increasing γ, the three-body energy is *quenched* considerably and *loses its sensitivity* with respect to the crystal structure. From this we anticipate that in the case of very dissimilar ions the main three-body contribution will arise from triangles ($\beta\beta\beta$), i.e., those formed by a large ion at the center and two of its *next*-nearest neighbors.

In addition to the types of isosceles triangles considered above, we will later also evaluate contributions to the three-body energy from nonisosceles triangles in the sodium chloride and cesium chloride configurations.

Next, we consider three-body interactions between the ions in *second order* of perturbation theory. In this case we have to evaluate, for an arbitrary triplet (abc)

FIG. 3. Relative first-order three-body energy $\Delta E_1/E_1^{(0)}$ as a function of the opening θ of isosceles triangles ($\beta'\beta\beta$), i.e., those with the *smaller* ion at the center, for $\beta R=1.5$ and $\gamma=(\beta'/\beta)^2=1, 2, 4, 10, 20,$ and 100.
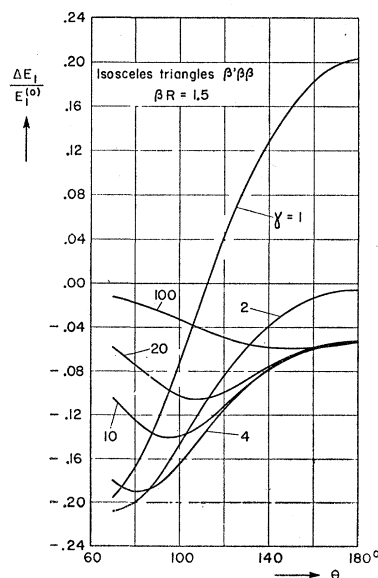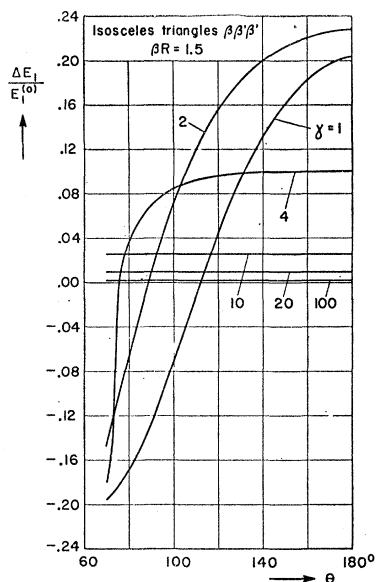
FIG. 4. Relative first-order three-body energy $\Delta E_1/E_1^{(0)}$ as a function of the opening θ of isosceles triangles $(\beta\beta'\beta')$, i.e., those with the *larger* ion at the center for $\beta R = 1.5$ and $\gamma = (\beta'/\beta)^2 = 1, 2, 4, 10, 20,$ and 100.

three-body interactions are strongly quenched; the three-body component of the crystal energy is then mainly due to triplets $(\beta\beta\beta)$ and the relation $\Delta E_1/E_1^{(0)} \approx \Delta E_2/E_2^{(0)}$ is again valid. By interpolation the relative first- and second-order three-body energies *will be taken as equal* over the whole range of values for βR and γ of alkali halide crystals.

Since the second-order pair energy $E_2^{(0)}$ for any triplet is negative, the symmetry properties of second-order three-body interactions are just the *reverse* of those in first order in that triangles with *large* opening θ are now favored. Accordingly, the stability of alkali-halide crystals will be found to depend on pair interactions (including the Madelung energy) and on a balance between first- and second-order three-body interactions for the different triplets in the cesium chloride and sodium chloride configurations.

DOUBLE-EXCHANGE CONTRIBUTIONS TO THREE-BODY ENERGY

The results of the previous section for the relative three-body interactions were obtained on the basis of a one-electron model for the ions. This implies that we take into account only contributions to the three-body energy due to exchange of a *single* pair of electrons between the same pair of ions. As the interionic distances decrease, it must be expected that effects due to multiple exchange become more important. Consequently, we must verify that the results of the previous section are not essentially changed if double exchange is taken into account. In particular, the symmetry properties of three-body interactions should be *stable* against double exchange.

To calculate double-exchange contributions it is sufficient to investigate the case $\gamma = 1$. Consider a triplet (abc) of identical Gaussian ions or atoms with *two*

effective electrons per ion (opposite spins), counterbalanced by nuclear charges of plus two. The zero-order wave function is (Slater determinant)

$$\Psi^{(0)} = [6!(1-\Delta^2_{abc})]^{-1/2} \det\{\varphi_a[1]\alpha_1\varphi_a[2]\beta_2$$
$$\times \varphi_b[3]\alpha_3\varphi_b[4]\beta_4\varphi_c[5]\alpha_5\varphi_c[6]\beta_6\}, \quad (10)$$

where 1–6 numbers the electrons and where α and β are spin functions (symbol β not to be confused with the Gaussian parameter). The atomic wave functions $\varphi(r)$ are again of the form (3), and Δ^2_{abc} is defined by (4). The perturbation Hamiltonian H'_{abc} is again a sum of perturbations between the three pairs of atoms, in this case with two electrons per atom.

The resulting expression for $\langle H'_{ab}\rangle/e^2$ is more complicated than the corresponding equation (5) for the single-exchange approximation; it can be written, noting that for identical atoms

$$G_{aa(b)} = G_{bb(a)}, \quad G_{ab(a)} = G_{ab(b)} \quad \text{and} \quad A_{aaab} = A_{bbba},$$

as

$$\langle H'_{ab}\rangle/e^2$$

$$= \frac{4}{R_{ab}} + \frac{1}{(1-\Delta^2_{abc})^2}\{-4G_{aa(b)}P + 8G_{ab(a)}Q$$

$$+ 4(1+[ab])G_{ac(b)}R + 2A_{abab}S$$

$$+ 2(1+[ab])A_{acab}T + 2A_{abba}U$$

$$+ 2(1+[ab])A_{aaab}V + 2(1+[ab])A_{acba}W$$

$$+ 2A_{abcc}X\}, \quad (11)$$

where the symbol $[ab]$ stands for the operation of permuting a and b, and where the symbols P to X are defined as follows:

$$P = 2 - 2\Delta^2_{ab} - 3\Delta^2_{ac} - 3\Delta^2_{bc} + 4\Delta_{ab}\Delta_{ac}\Delta_{bc}$$
$$+ \Delta^2_{ab}\Delta^2_{bc} + \Delta^2_{ab}\Delta^2_{ac} + 2\Delta^2_{ac}\Delta^2_{bc} + \Delta^4_{ac} + \Delta^4_{bc}$$
$$- 2\Delta_{ab}\Delta_{ac}\Delta^3_{bc} - 2\Delta_{ab}\Delta_{bc}\Delta^3_{ac};$$

$$Q = \Delta_{ab} - \Delta_{ac}\Delta_{bc} - \Delta^3_{ab} - \Delta_{ab}\Delta^2_{bc} - \Delta_{ab}\Delta^2_{ac}$$
$$+ \Delta_{ac}\Delta^3_{bc} + \Delta_{bc}\Delta^3_{ac} + 3\Delta^2_{ab}\Delta_{ac}\Delta_{bc} - 2\Delta_{ab}\Delta^2_{ac}\Delta^2_{bc};$$

$$R = \Delta_{ac} - \Delta_{ab}\Delta_{bc} - \Delta^2_{ab}\Delta_{ac} - \Delta^2_{bc}\Delta_{ac} - \Delta^3_{ac}$$
$$+ \Delta_{ab}\Delta^3_{bc} + \Delta^3_{ab}\Delta_{bc} + 3\Delta_{ab}\Delta^2_{ac}\Delta_{bc} - 2\Delta^2_{ab}\Delta_{ac}\Delta^2_{bc};$$

$$S = 2 - 2\Delta^2_{ac} - 2\Delta^2_{bc} - \Delta^2_{ab} + 2\Delta_{ab}\Delta_{ac}\Delta_{bc} + \Delta^2_{ac}\Delta^2_{bc};$$

$$T = -2\Delta_{bc} + \Delta_{ab}\Delta_{ac} + 2\Delta^3_{bc} + \Delta^2_{ab}\Delta_{bc}$$
$$+ \Delta^2_{ac}\Delta_{bc} - 3\Delta_{ab}\Delta_{ac}\Delta^2_{bc};$$

$$U = -1 + \Delta^2_{ac} + \Delta^2_{bc} + 2\Delta^2_{ab} - 4\Delta_{ab}\Delta_{ac}\Delta_{bc} + \Delta^2_{ac}\Delta^2_{bc};$$

$$V = -\Delta_{ab} + \Delta_{ac}\Delta_{bc} - \Delta_{ac}\Delta^3_{bc} + \Delta_{ab}\Delta^2_{bc};$$

$$W = \Delta_{ac} + \Delta_{ab}\Delta_{ac} - 2\Delta^2_{ab}\Delta_{ac} - 2\Delta_{ac}\Delta^2_{bc} - \Delta^3_{ac}$$
$$+ 3\Delta_{ab}\Delta_{bc}\Delta^2_{ac};$$

and

$$X = \Delta_{ac}\Delta_{bc} - \Delta_{ab}\Delta^2_{bc} - \Delta_{ab}\Delta^2_{ac} + \Delta^2_{ab}\Delta_{ac}\Delta_{bc}. \quad (12)$$
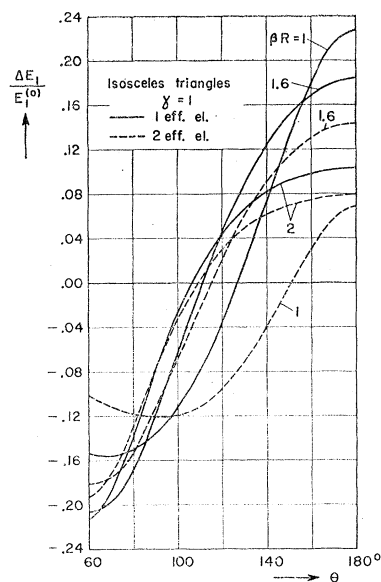
FIG. 5. Relative first-order three-body energy $\Delta E_1/E_1^{(0)}$ as a function of the opening θ of isosceles triangles ($\gamma = 1$) for $\beta R = 1.0$, 1.6, and 2.0, for one and for two effective electrons.

The equations for $\langle H'_{ac}\rangle/e^2$ and $\langle H'_{bc}\rangle/e^2$ are obtained from (11) and (12) by cyclic permutations.

The first-order energy for the pair (ab), *without c* present, is then given by (11) with atom c removed to infinity. The result, corresponding to (6), is

$$\langle H'_{ab}\rangle^{(0)}/e^2 = \frac{4}{R_{ab}}$$

$$-\frac{4}{(1-\Delta^2_{ab})}\{2G_{aa(b)} - 2\Delta_{ab}G_{ab(a)} - (A_{abab} - A_{aabb})\}$$

$$+\frac{2}{(1-\Delta^2_{ab})^2}[\Delta^2_{ab}A_{abab} + A_{aabb} + 2\Delta_{ab}A_{aaab}]. \quad (13)$$

By comparing (6) and (13) we see that the first two terms of (13) represent four times the single-exchange first-order energy between a and b; the remainder constitutes an interference effect between the electron pairs on the different atoms. The interactions between a and c, or those between b and c, follow again from (13) by cyclic permutations.

In Fig. 5 the results for $\Delta E_1/E_1^{(0)}$ are given for $\beta R = 1.0$; 1.6 and 2.0, as a function of the opening θ of isosceles triangles, both for one and for two effective electrons. We draw the following conclusions:

(a) *No qualitative changes occur for* $\Delta E_1/E_1^{(0)}$, as a function of θ, if double exchange is taken into account. In particular, the symmetry properties of the three-body interactions remain *the same* even for values as small as $\beta R = 1$.

(b) Double exchange *quenches* $\Delta E_1/E_1^{(0)}$ both at small and at large openings of the triangles, but the quenching effect decreases rapidly with increasing βR.

These results confirm validity of the single exchange approximation for rare-gas crystals ($\beta R \geqslant 2$).

(c) The double-exchange analysis supports the assumed similarity between stability of rare-gas and alkali-halide crystals.

In view of these results, it is justified to carry out the stability analysis on the basis of a *single-exchange* approximation.

DETERMINATION OF GAUSSIAN PARAMETERS FOR ALKALI HALIDES

The values of the Gaussian parameter β for rare-gas atoms can be determined from pair potential functions[13] at large and at small interatomic distances. For alkali-halide ions such a method cannot be used, since pair potentials between the ions are unknown. Therefore, a different procedure for estimating the Gaussian parameters β, β' or β, γ must be followed. We expect that the β value for each cation will be somewhat larger than that for the corresponding isoelectronic rare gas atom, and for each anion that it is somewhat smaller than this value.

To estimate such differences, experimental values for the molar diamagnetic susceptibilities of alkali-halide ions and rare-gas atoms[17] were used to evaluate β parameters of the ions. Since the susceptibility χ of an atom or ion with one effective electron is proportional to $\langle r^2\rangle$, i.e., proportional to β^{-2} for a Gaussian distribution, we have the following relation

$$(\beta_{\text{ion}}/\beta_{\text{atom}})^2 = \chi_{\text{atom}}/\chi_{\text{ion}}. \quad (14)$$

The β values for ions were calculated from (14) by comparing each ion with its corresponding isoelectronic rare gas atom, using for the atoms the β parameters obtained from pair potentials.[18,13] The resulting values are given in Table II together with those of the rare-gas atoms. In addition, we give in Table III values of γ and βR for the alkali-halide crystals; R denotes the nearest-neighbor distance in the lattice and β represents the larger ion.

The values in the two tables should be viewed primarily in relation to each other and to the rare-gas crystals, for which the values of βR are 2.0 (xenon), 2.1 (krypton), 2.4 (argon), and 3.4 (neon). We have included the calculated parameters for lithium halides,

TABLE II. Values obtained with (14) for Gaussian parameter β in units 10^8 cm^{-1}, for alkali-halide ions, and compared with those of rare-gas atoms.

He	1.59	Ne	1.07	A	0.623	Kr	0.532	Xe	0.454
Li$^+$	2.60	Na$^+$	1.162	K$^+$	0.718	Rb$^+$	0.600	Cs$^+$	0.503
		F$^-$	0.936	Cl$^-$	0.558	Br$^-$	0.479	I$^-$	0.419

[17] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1957), Chap. 9.
[18] L. Jansen and R. T. McGinnies, Phys. Rev. **104**, 961 (1956).

TABLE III. Values obtained with (14) for the dimensionless parameters βR and $\gamma = (\beta'/\beta)^2$ for alkali-halide crystals; R denotes the nearest-neighbor distance and β represents the larger ion.

Alkali halide	βR	γ	Alkali halide	βR	γ
LiF	1.88	7.72	LiBr	1.325	29
NaF	2.16	1.54	NaBr	1.43	5.88
KF	1.91	1.70	KBr	1.58	2.25
RbF	1.69	2.43	RbBr	1.64	1.57
CsF	1.51	3.46	CsBr	1.78	1.10
LiCl	1.44	22	LiI	1.26	38
NaCl	1.57	4.34	NaI	1.35	7.69
KCl	1.75	1.66	KI	1.48	2.94
RbCl	1.83	1.16	RbI	1.54	2.05
CsCl	1.79	1.23	CsI	1.66	1.44

although it is only relevant to mention that their γ values are high.

THE STABILITY OF ALKALI-HALIDE CRYSTALS

We will now apply the results of the previous sections to the stability of alkali-halide crystals. As a simplification, we limit ourselves to the absolute zero of temperature and neglect the effect of zero-point energy on stability, so that we only have to compare the *static* lattice energies of the cesium chloride and the sodium chloride configurations for the different alkali halides.

Consider a crystal of N cations and N anions; the static lattice energy, $E(r_1, r_2, \cdots, r_{2N})$, is defined as the difference between the energy of the crystal, for a fixed configuration r_1, r_2, $\cdots$, r_{2N} of nuclei, and the energy of the $2N$ constituents at infinite separations and at absolute zero temperature. We write the lattice energy formally as a series of terms depending upon the position coordinates of increasing numbers of ions, as follows

$$E(r_1, r_2, \cdots, r_{2N}) = E\{2\} + E\{3\} + E\{4\} + \cdots, \quad (15)$$

where $E\{2\}$ contains all terms of E which depend on the coordinates of only two ions; in $E\{3\}$ all terms are collected which are simultaneously functions of the coordinates of three ions, etc. We assume that this expansion may be terminated with the three-particle function $E\{3\}$ for molecular crystals and ionic solids.

Expressions for the components $E\{2\}$, $E\{3\}$, etc., of E in terms of the interactions between the ions can easily be given. Evidently, $E\{2\}$ is just the sum of interactions for the *isolated pairs* of ions in the crystal. Further, $E\{3\}$ is the limiting value of $E - E\{2\}$ if all simultaneous interactions between more than three ions are discarded, i.e.,

$$E\{3\} = \sum_{a<b<c} [E(abc) - \{E^{(0)}(ab) + E^{(0)}(ac) + E^{(0)}(bc)\}]$$

$$\equiv \sum_{a<b<c} \Delta E(abc), \quad (16)$$

where $E(abc)$ denotes the total interaction energy for the *isolated* triplet (abc) and $E^{(0)}(ab)$ the interaction for the *isolated* pair (ab); the summations extend over all

possible triplets. The pair interactions $E^{(0)}(ab)$ and the triplet interactions $\Delta E(abc)$ are evaluated in first and second orders of perturbation theory. We write $E^{(0)} = E_1^{(0)} + E_2^{(0)}$ and $\Delta E = \Delta E_1 + \Delta E_2$ for any pair or triplet of ions; the subscripts 1 and 2 denote the orders of perturbation, as in the previous sections.

We first consider the *pair energy* $E\{2\}$ for the crystal. Since accurate theoretical expressions for the pair interactions between ions are not available, we use the empirical information that the *total pair energy* of alkali-halide crystals may be calculated with a model of electrostatic interactions between *point* charges for the ions, supplemented by first-order repulsions between the closed shells. We remark that the van der Waals (second-order) interactions between the ions are only indirectly represented in this model. Since we have ascribed the structure dependence of the repulsive parameters, analyzed by Tosi and Funi,[8] to the effect of *three-body* interactions, we write, accordingly, the total pair energy $E\{2\}$ for each alkali halide and either crystal structure as a sum of Madelung energy M and of the total first-order repulsion between the ions, i.e., as

$$E\{2\} = M + \sum_{a<b} E_1^{(0)}(ab). \quad (17)$$

Further, let $\Delta E = \Delta E_1 + \Delta E_2$ represent the three-body energy for an arbitrary triplet and $\Delta E_1/E_1^{(0)}$, $\Delta E_2/E_2^{(0)}$ the relative first- and second-order three-body interactions. With the assumption $\Delta E_1/E_1^{(0)} \approx \Delta E_2/E_2^{(0)}$ we can now write

$$\Delta E = (\Delta E_1/E_1^{(0)}) E_1^{(0)} + (\Delta E_2/E_2^{(0)}) E_2^{(0)}$$

$$\approx (\Delta E_1/E_1^{(0)})(E_1^{(0)} + E_2^{(0)}), \quad (18)$$

where $E_1^{(0)} + E_2^{(0)} = E^{(0)}$ is the total (first-plus second-order) pair energy of the triplet. It is important to note, from (18), that in this case *the van der Waals pair interactions $E_2^{(0)}$ must explicitly be taken into account.* The three-body crystal energy $E\{3\}$ is the sum of (18) over all possible triplets of ions.

TABLE IV. Numbers and types of triangles *per ion* in the sodium chloride configuration. The sides of the triangles are in units of nearest neighbor distance; θ is the angle between R_{ab} and R_{ac}.

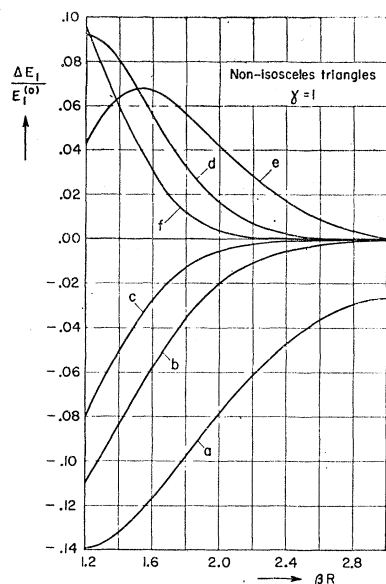| Type	Number per ion	R^2_{ab}	R^2_{ac}	R^2_{bc}	$\cos^2\theta$	θ
$A_0 C_1 C_1$	12	1	1	2	0	90°
$(C_0 A_1 A_1)$	3	1	1	4	1	180°
$A_0 A_2 A_2$	8	2	2	2	1/4	60°
$(C_0 C_2 C_2)$	12	2	2	4	0	90°
	24	2	2	6	1/4	120°
	6	2	2	8	1	180°
$A_0 C_1 A_2$	24	1	2	3	0	90°
$(C_0 A_1 C_2)$	24	1	2	5	1/2	135°
$A_0 C_1 C_3$	24	1	3	6	1/3	125° 15'
$(C_0 A_1 A_3)$						
$A_0 A_2 C_3$	48	2	3	5	0	90°
$(C_0 C_2 A_3)$	24	2	3	9	2/3	144° 44'

FIG. 6. Relative first-order three-body energy $\Delta E_1/E_1^{(0)}$ for the special case $\gamma=1$ for *nonisosceles* triangles. In the notation of Tables IV and V, curve (b) refers to triangles (1, 2, 3; $\theta=90°$), curve (c) to (1, 8/3, 11/3; $\theta=90°$), curve (d) to (1, 2, 5; $\theta=135°$), curve (e) to (1, 4/3, 11/3; $\theta=125°$ 15′), and curve (f) to (1, 8/3, 19/3; $\theta=144°$ 44′). For comparison with *isosceles* triangles, curve (a) refers to the type (1, 1, 2; $\theta=90°$).

To evaluate $E\{3\}$ for the cesium chloride and the sodium chloride structures, we first classify the different triangles formed by a central ion and two neighbors of the first few shells in the two configurations. Before, we have indicated such triangles by the corresponding triplet of Gaussian parameters, but for what follows a more specific notation is needed. We denote a cation by C, an anion by A, and add subscripts 0, 1, 2, to distinguish between different shells around the central ion. The subscript zero refers to the central cation or anion.

In Tables IV and V, the numbers *per ion* and the types of different triangular configurations are given for the sodium chloride and cesium chloride structures. The sides R_{ab}, R_{ac}, and R_{bc} are expressed in units of nearest-neighbor distance R; θ is the angle between R_{ab} and R_{ac}. The type of triangle $A_0C_1A_2$, for example, denotes a triangle formed by a central anion, a cation

TABLE V. Numbers and types of triangles *per ion* in the cesium chloride configuration. The sides of the triangles are in units of nearest-neighbor distance; θ is the angle between R_{ab} and R_{ac}.

Type	Number per ion	R^2_{ab}	R^2_{ac}	R^2_{bc}	$\cos^2\theta$	θ
$A_0C_1C_1$	12	1	1	4/3	1/9	70° 32′
$(C_0A_1A_1)$	12	1	1	8/3	1/9	109° 28′
	4	1	1	4	1	180°
$A_0A_2A_2$	12	4/3	4/3	8/3	0	90°
$(C_0C_2C_2)$	3	4/3	4/3	16/3	1	180°
$A_0A_3A_3$	8	8/3	8/3	8/3	1/4	60°
$(C_0C_3C_3)$	12	8/3	8/3	16/3	0	90°
	24	8/3	8/3	8	1/4	120°
	6	8/3	8/3	32/3	1	180°
$A_0A_2A_3$	24	4/3	8/3	4	0	90°
$(C_0C_2C_3)$	24	4/3	8/3	20/3	1/2	135°
$A_0C_1A_2$	24	1	4/3	11/3	1/3	125° 15′
$(C_0A_1C_2)$						
$A_0C_1A_3$	48	1	8/3	11/3	0	90°
$(C_0A_1C_3)$	24	1	8/3	19/3	2/3	144° 44′

of the first shell and an anion belonging to the second shell of neighbors. As is seen from the tables, the first two types of triplets in the sodium chloride structure and the first three types of triplets in the cesium chloride structure form isosceles triangles. The remaining types of triangles have three different sides; we will first verify that the contributions to the three-body energy due to these nonisosceles triangles are small, so that we then may restrict ourselves to isosceles triangles only.

We have determined the relative first-order three-body energy $\Delta E_1/E_1^{(0)}$ as a function of βR for the congruent types of triangles $A_0C_1A_2$ (sodium chloride) and $A_0A_2A_3$ (cesium chloride) as well as for the types $A_0C_1A_2$ and $A_0C_1A_3$ (cesium chloride). For simplicity, we considered only the case $\gamma=1$. The results are given in Fig. 6. For comparison, curve (a) of Fig. 6 refers to an *isosceles* triangle with $\theta=90°$. We draw the following conclusions:

(i) $\Delta E_1/E_1^{(0)}$ is quenched for $\theta=90°$ as the third ion is moved away from the other two; this is apparent from curves (a), (b), and (c). Also, $\Delta E_1/E_1^{(0)}$ decreases rapidly with increasing βR.

(ii) Contributions from nonisosceles triangles in either structure *tend to cancel each other*. For example, consider the type $A_0C_1A_2$ (sodium chloride); there are 24 such triangles with $\theta=90°$ [curve (b)] and 24 with $\theta=135°$ [curve (d)]. These two contributions are practically equal and of opposite sign over the whole range of values of βR. In the same way, considering the types $A_0C_1A_2$ and $A_0C_1A_3$ (cesium chloride), we note that there are 24 triangles with $\theta=125°$ 15′ [curve (e)], and 24 with $\theta=144°$ 44′ [curve (f)], which practically cancel against 48 triangles with $\theta=90°$ [curve (c)]. The same considerations apply to the types $A_0C_1C_3$, $A_0A_2C_3$, (sodium chloride) and to the type $A_0A_2A_3$ (cesium chloride).

It is thus seen that the contributions from nonisosceles triangles are *small, of the same order in the two structures and, moreover, that they tend to cancel each other in either structure because of symmetry properties of three-body interactions.*

We will now undertake the stability analysis, restricting ourselves to the *isosceles* triangles of Table IV (sodium chloride structure) and of Table V (cesium chloride structure). A number of qualitative features of the differences between the two structures with respect to stability can already be obtained by comparing triangles of Tables IV and V and applying symmetry properties of three-body interactions. However, we will postpone a more general discussion until after the complete numerical results have been presented.

The stability analysis is carried out in the following four steps:

(A) *For each alkali halide and for both structures we determine the total three-body energy (16) for N cations and N anions.* The values of γ and βR are taken from

Table III. To determine ΔE for each triangle from (18), we must know its *total* pair energy, including contributions from van der Waals interactions. For rare-gas crystals (see I) a pair potential function is taken as basis, e.g., a Lennard-Jones (12,6) potential, placing nearest neighbors at a distance where the potential has its minimum. For alkali halides such pair potentials[19] are not known with precision. We estimate that, on the basis of a Lennard-Jones (12,6) potential, the nearest-neighbor distance may be taken between 0.85σ and 0.90σ, where σ is the distance for zero potential. The ratio between repulsive and attractive interactions for such a pair varies between -2.7 and -1.9. This implies that $E_1^{(0)}+E_2^{(0)}$ for a pair of nearest neighbors varies between $0.63\ E_1^{(0)}$ and $0.47\ E_1^{(0)}$. We will write for the *total pair energy* of the triplet $E_1^{(0)}(1-b)$, with b between 0.4 and 0.6, approximately.

On the other hand, if next-nearest neighbors are at distances comparable to the nearest-neighbor separation in rare gas crystals, then the relation $E_2^{(0)}\approx-2E_1^{(0)}$ holds, so that $E_1^{(0)}+E_2^{(0)}\approx-E_1^{(0)}$ in this case. Contributions from triangles at much larger distances will be neglected.

On the basis of these estimates we can evaluate ΔE for each triplet in terms of its *total first-order pair energy* $E_1^{(0)}$. To sum over the different triangles we must relate their first-order energies. Let α_1 denote the pair repulsion between nearest neighbors, α_2 the repulsion

TABLE VI. Total pair repulstion (column 1), total three-body energy involving nearest neighbors (column 2), total three-body energy involving next-nearest neighbors (column 3), for the alkali halides in the sodium chloride configuration. All results are expressed in units of nearest-neighbor repulsion α_1, except those in column 2, where the unit is $\alpha_1(1-b)$. The parameter b stands for the ratio between first- and second-order pair interactions for a triplet of nearest neighbors; $b\approx0.5$ approximately.

| | | Sodium chloride configuration | |
| | | Three-body energy | |
Alkali halide	Pair repulsion	$A_0C_1C_1;$ $C_0A_1A_1$	$A_0A_2A_2;$ $C_0C_2C_2$
LiF	11.68	−4.46	4.36
NaF	6.30	−1.91	0.24
KF	6.82	−2.41	0.64
RbF	8.09	−3.07	1.48
CsF	10.21	−3.88	2.64
LiCl	37.23	−7.37	18.46
NaCl	11.06	−4.44	3.32
KCl	7.20	−2.81	0.83
RbCl	6.96	−2.92	0.72
CsCl	7.03	−2.96	0.53
LiBr	55.33	−8.10	27.47
NaBr	14.56	−5.40	5.06
KBr	8.31	−3.23	1.47
RbBr	7.55	−3.18	1.04
CsBr	7.16	−3.13	0.83
LiI	75.50	−8.48	37.59
NaI	18.49	−6.21	7.13
KI	9.65	−3.64	2.20
RbI	8.30	−3.37	1.39
CsI	7.47	−3.22	1.00

[19] Cf. Y. P. Varshni and R. C. Shukla [J. Chem. Phys. **35**, 582 (1961)] for detailed references.

TABLE VII. Total pair repulsion (column 1), total three-body energy involving nearest neighbors (column 2), total three-body energy involving next-nearest neighbors (column 3) and third neighbors (column 4), for the alkali halides in the cesium chloride configuration. All results are expressed in units of nearest-neighbor repulsion α_1, except those in column 2, where the unit is $\alpha_1(1-b)$. The parameter b stands for the ratio between first- and second-order pair interactions for a triplet of nearest neighbors; $b\approx0.5$ approximately.

| | | Cesium chloride configuration | | |
| | | Three-body energy | | |
Alkali halide	Pair repulsion	$A_0C_1C_1;$ $C_0A_1A_1$	$A_0A_2A_2;$ $C_0C_2C_2$	$A_0A_3A_3;$ $C_0C_3C_3$
LiF	24.60	−10.87	5.47	···
NaF	10.07	−7.84	0.44	···
KF	10.78	−8.53	0.82	0.30
RbF	12.60	−9.47	1.81	0.39
CsF	15.53	−10.60	3.44	0.98
LiCl	61.20	−15.12	24.91	8.05
NaCl	17.55	−11.19	4.20	1.10
KCl	11.16	−8.90	1.14	0.19
RbCl	10.75	−8.78	0.92	0.09
CsCl	10.83	−8.82	0.96	0.11
LiBr	86.41	−16.30	37.47	13.22
NaBr	22.41	−12.44	6.68	2.15
KBr	12.59	−9.58	1.95	0.49
RbBr	11.44	−9.15	1.34	0.27
CsBr	10.94	−8.91	1.06	0.11
LiI	115.02	−16.88	51.58	18.78
NaI	28.17	−13.50	9.55	3.31
KI	14.45	−10.27	2.90	0.88
RbI	12.46	−9.59	1.91	0.50
CsI	11.33	−9.11	1.29	0.24

between next-nearest neighbors and α_3 that between third neighbors in the crystal. We equate α_2/α_1 and α_3/α_1 to the corresponding ratios between first-order interactions in the Gaussian model. Since $E_1^{(0)}$ for any triplet considered is a function of α_1, α_2, and α_3, we can express in this way $E_1^{(0)}$ for each triplet as a function of α_1 only.

(B) *The total first-order pair energy* $E\{2\}$ *is then evaluated* from (17) by adding to the Madelung energy the sum of all pair repulsions as a function of α_1, using Gaussian ratios for distant neighbors.

(C) From (A) and (B) we obtain the *sum of all pair and triplet interactions* as a function of α_1 for the two structures. This sum, for the stable structure, is put equal to the experimental value of the lattice energy as determined by the Born-Haber cycle. We use this equality to determine the nearest-neighbor repulsion α_1.

(D) With the value of α_1 obtained from (C), we calculate the *lattice energy of the other structure*. The energy difference between the two structures is then used to evaluate also transition pressures from the sodium chloride to the cesium chloride structure.

The results of steps (A) and (B) for all alkali halides in the sodium chloride and cesium chloride configurations are reported in Tables VI and VII, respectively. The first column of either Table gives the total pair repulsion in units of the nearest-neighbor repulsion α_1. In the second column we list the total three-body contributions from $A_0C_1C_1$ and $C_0A_1A_1$ triangles, whereas the third column gives the total three-body

TABLE VIII. Difference in lattice energy, ΔE, in kcal/mole between the cesium chloride and the sodium chloride configurations for the alkali halides. Also given are calculated transition pressures, P_t(calc) in kbar compared with the results of the Born-Mayer-Jacobs theory $P_t(B-M)$, and experimental values P_t(exp). The first column gives the values for the parameter b.

Alkali halide	b	ΔE kcal/mole	P_t(calc) kbar	$P_t(B-M)$ kbar	P_t(exp) kbar
LiF	0.6	33.3	1.060	300	...
NaF	0.6	7.5	158	200	...
KF	0.6	6.0	83	88	...
RbF	0.4	2.2	25	68	9–15[a]
CsF	0.4	3.2	31	35	(not observed)[a]
LiCl	0.6	14.4	221	140	...
NaCl	0.6	8.1	95	74	...
KCl	0.5	2.1	18	74	19.6
RbCl	0.5	1.05	7.7	39	4.9
CsCl	0.4	−0.6		(not calc)	
LiBr	0.6	11.0	140	105	...
NaBr	0.6	7.8	78	53	...
KBr	0.5	2.3	17	59	18
RbBr	0.5	0.94	6.1	30	4.5–5.0
CsBr	0.4	−0.82		(not calc)	
LiI	0.6	6.9	67	68	...
NaI	0.6	5.7	44	44	...
KI	0.6	2.8	17	49	17.85
RbI	0.5	0.9	4.8	22	4.0
CsI	0.4	−0.95		(not calc)	

[a] See Ref. 21. New experiments on cesium fluoride have been announced by these authors.

interactions for triangles $C_0C_2C_2$ and $A_0A_2A_2$ in either structure. Finally, in the fourth column of Table VII we list the contributions from triangles $A_0A_3A_3$ and $C_0C_3C_3$ in the cesium chloride configuration. From Tables VI and VII we draw the following main conclusions:

(I) The three-body interactions for triplets involving *nearest neighbors* ($A_0C_1C_1$ and $C_0A_1A_1$) increase the *attractive* forces in either structure. The contribution is larger for the *cesium chloride* configuration, *which is thus favored by these types of triangles.*

(II) The three-body interactions for triplets involving *next-nearest neighbors* ($A_0A_2A_2$ and $C_0C_2C_2$) in the sodium chloride structure, and next-nearest as well as third neighbors in the cesium chloride structure ($A_0A_2A_2$, $C_0C_2C_2$, $A_0A_3A_3$ and $C_0C_3C_3$) increase the *repulsive* forces in either structure. The contribution is smaller (less repulsive) for the *sodium chloride* configuration, *which is thus favored by these types of triangles.*

(III) When the ions become more dissimilar in size, i.e., when γ increases, the three-body interactions involving *next-nearest neighbors* become increasingly more important with respect to those involving first neighbors.

(IV) In addition to the difference in Madelung energy between the two structures, *the stability is determined by a balance between pair repulsions, three-body attractive and three-body repulsive forces;* these different components of the crystal energy depend on the values of βR and γ. For large values of γ we predict the sodium chloride structure to be the stable one. As will be shown, this influence of γ explains the difference in crystal

structure between cesium fluoride ($\gamma \approx 3.5$) and that of the other cesium halides (γ between 1.1 and 1.4).

(V) All the above conclusions are independent of α_1, the pair repulsion between nearest neighbors, and of the parameter b which measures the ratio between second-order and first-order pair interactions for a triplet of nearest neighbors.

Finally, following steps (C) and (D) of the analysis, we determine the difference in static lattice energy between the sodium chloride and the cesium chloride configurations for the alkali halides. In addition, we estimate the transition pressures for those halides which exhibit sodium chloride structure at normal pressure, following the simplified treatment given by Born and Huang.[20]

In Table VIII, the numerical results are given for the difference in lattice energy ΔE between the cesium chloride and the sodium chloride structures. A *positive* value of ΔE implies that the *sodium chloride* structure is the stable one. Also included in the table are values for the transition pressure, P_t(calc), the corresponding results of the Born-Mayer-Jacobs theory $P_t(B-M)$, and the experimental[21,22] values, P_t(exp). The precise numerical values for the paramber b are not of importance for the *sign* of the difference in lattice energy. However, the transition pressures are a sensitive function of b. The values listed in Table VIII give the best agreement with experimental results on transition pressures. It is important to observe that b varies regularly and in the same manner for all the alkali-halide crystals.

DISCUSSION OF RESULTS

It is seen from the results reported in Table VIII that by introducing three-body exchange interactions between the ions, *all the main aspects of the stability problem for alkali-halide crystals can be derived on a quantitative basis.* Specifically, the theory accounts for the stability of the cesium chloride configuration for cesium chloride, bromide, and iodide. Moreover, the theory reproduces the pressure values of experimentally observed transitions from the sodium chloride to the cesium chloride configuration. Further, it is of particular interest to note that the theory agrees with recent experimental information[22] according to which rubidium fluoride is *less stable* in the sodium chloride structure than cesium fluoride.

Considering the values of the parameter b, which stands for an average ratio between second- and first-order pair interactions for a triplet of nearest neighbors, it is seen that these vary regularly and in the *same* manner for all alkali halides; the limiting values of 0.6

[20] Reference 1, Chap. III, Eqs. (13.18) and (13.19).
[21] P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, Ltd., London, 1952).
[22] G. J. Piermarini and C. E. Weir, J. Chem. Phys. **37**, 1887 (1962).

and 0.4 can be explained by analogy with potential functions between rare-gas atoms. To illustrate the sensitivity of the results with respect to changes in b, we find that, taking $b=0.5$ instead of 0.6 for potassium fluoride and iodide, the values for ΔE and P_t change to 3.8 kcal/mole, 53 kbar, 2.2 kcal/mole, 13.5 kbar, respectively.

The *relative magnitude* of the total three-body interactions, with respect to the crystal energy of the stable structure, lies between -1.6 and $+3.3\%$ for the fluorides, between -2.8 and $+3.6\%$ for the chlorides, between -2.2 and $+3.5\%$ for the bromides, and between -2.6 and $+2.3\%$ for the iodides. The total pair repulsion varies between 7 and 18% of the crystal energy, in good agreement with the Born-Mayer theory.

Other attempts have been undertaken in the literature to introduce many-body interactions in alkali halide crystals; these have, however, no bearing on stability. Apart from Löwdin's first-order calculations,[9] which we have already discussed, we mention a semi-classical analysis by Dick and Overhauser,[23] and by Dick,[24] based on electrostatic interactions involving "exchange charges" in terms of which the first-order repulsion between two closed-shell atoms was interpreted. Four-body interactions are then introduced by considering electrostatic forces between two exchange charges associated with two *nonoverlapping* pairs of atoms or ions; three-body interactions arise from forces between an exchange charge and *distant* ions. Finally, Colwell[25] has attempted a detailed analysis for the specific case of cesium chloride in terms of the various possible contributions to the crystal field, starting from explicit expressions for the electron wave functions. Unfortunately, it is impossible to estimate the reliability of such a calculation.

There are two aspects of the theory of alkali-halide stability, presented in this paper, which we like to emphasize. *First*, the essential simplicity of the original Born-Mayer theory, which has been so successful in interpreting many properties of alkali-halide and other ionic solids, is retained. The reason why the Born-Mayer theory fails to account for stability of the cesium chloride structure is that the gain in Madelung energy in going from the sodium chloride to the cesium chloride configuration is overcompensated by an increase in pair-repulsion energy for all alkali halides. Three-body exchange interactions for triplets of smallest dimensions in the two structures introduce a net attraction in favor of the cesium chloride structure, which effect in some cases suffices to render this configuration the stable one. The three-body interactions are of short range, strongly structure-dependent, and they exhibit simple symmetry properties. *Second*, the stability problems of rare-gas crystals and of alkali-halide crystals are resolved *on the same physical basis*. For ions of comparable size, i.e., for values of γ not too different from one, the ions can be replaced by the corresponding isoelectronic rare-gas atoms. Because of the compression of the crystal due to the Madelung energy, nearest neighbors repel each other. Compared with rare-gas crystals, *the sign of the three-body interactions is now reversed*. For ions of very dissimilar size, i.e., for values of γ much larger than one, we can, in the limit, replace the smaller ion by a point charge and the larger one by the corresponding rare-gas atom. The sign of the three-body interactions for the larger ions, *which dominate stability*, in then *the same as in the case of rare-gas crystals*. It must be expected that the stability of other classes of ionic solids, e.g., the zincblende-wurtzite relative stability, can be explained on the same basis.

[23] B. G. Dick, Jr. and A. W. Overhauser, Phys. Rev. 112, 90 (1958).
[24] B. G. Dick, Jr., Phys. Rev. 129, 1583 (1963).
[25] J. F. Colwell, thesis, Cornell University, 1960 (unpublished).