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Stability of Crystals of II-VI and III-V Compounds in Terms of Three-Ion Interactions

ERMINIO LOMBARDI* AND LAURENS JANSEN
International Division, Battelle Memorial Institute, Geneva, Switzerland

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By extending the theory developed in previous publications for the stability of rare-gas and alkali-halide crystals, it is shown that the stability of crystals of II-VI and III-V compounds whose ions are isoelectronic with rare-gas atoms is explained in terms of three-ion exchange interactions, without involving the concept of covalency. The analysis is based on a first- and second-order perturbation calculation, starting from complete ionicity in zeroth order of approximation. As in the case of rare-gas and alkali-halide crystals, Gaussian-type effective electron wave functions are used, taking into account the different size of anion and cation for each compound. It is shown that the theory accounts for all observed regularities on a quantitative basis. The occurrence of the sphalerite ($B3$) and wurtzite ($B4$) structures is explained; in addition, it is shown that the relative stability of these two structures is determined uniquely by three-ion interactions. By combining a Born-Mayer description for ionic solids with three-ion exchange interactions, general rules can be given which determine the relative stability of the four structures $B1$ (sodium chloride), $B2$ (cesium chloride), $B3$ (sphalerite), and $B4$ (wurtzite) observed with compounds of the type RX.

INTRODUCTION

THE general problem of interpreting the stability of observed crystal structures for compounds of the type RX in terms of interactions between the constituent atoms or ions has received extensive attention in the literature ever since Hund[1] first considered their stability on the basis of an ionic model and, almost simultaneously, Lennard-Jones and Ingham[2] compared the lattice energies of cubic configurations for crystals of the rare-gas atoms.

In both cases, only central forces between the ions or atoms were assumed. In Hund's model, the ions interact electrostatically as point charges; the solid is prevented from collapsing by an empirical repulsive potential at short distances, where the closed shells of nearest ions in the solid penetrate appreciably. Hund also considered the possibility of repulsion, or attraction, between second neighbors in the crystal. The calculations by Lennard-Jones and Ingham were based on a pair potential between rare-gas atoms consisting of a short-range repulsion and an attraction of longer range, varying with interatomic distance R as R^{-p} and R^{-m}, respectively ($p>m$).

On the basis of central forces, the *structure-dependent* parameters, determining the relative stability of different possible structures, arise from lattice sums over functions of the distance between a central atom (ion) and the remaining atoms (ions) of the solid. The Madelung constant, which characterizes the total electrostatic interaction between point charges of the ions, is one example. Further, in Hund's analysis, it was found that no essential structure dependence is lost by limiting the repulsions to nearest neighbors only. As a result, the coordination number Z of the lattice occurs directly in the expression for the static lattice energy.

If the repulsion between nearest ions (cation-anion) in the lattice is assumed to vary with inter-ionic distance R as R^{-p}, then the relative stability of ionic solids, at the absolute zero of temperature, is determined uniquely by the magnitude of the parameter $(M^p/Z)^{1/(p-1)}$, where M is the Madelung constant and Z the coordination number of the lattice; we have here neglected the effect of zero-point energy. A classification of relative stability for ionic solids of the type RX, with the exponent p of the repulsion as a variable, can then readily be given for the observed structures *sodium chloride* ($B1$, two interpenetrating face-centered cubic lattices; $Z=6$), *cesium chloride* ($B2$, two interpenetrating simple-cubic lattices; $Z=8$), *sphalerite* ($B3$, two interpenetrating face-centered cubic lattices; $Z=4$), and *wurtzite* ($B4$, two interpenetrating hexagonal close-packed lattices; $Z=4$). For $p>33$ the sequence in order of decreasing stability is $B2$, $B1$, $B3$ ($B4$); for $9.5<p<33$ the sequence is $B1$, $B2$, $B3$ ($B4$); for $6.3<p<9.5$ one obtains $B1$, $B3$ ($B4$), $B2$, whereas for $p<6.3$ the sequence reads $B3$ ($B4$), $B1$, $B2$. No distinction can be made between the stability of the $B3$ and $B4$ structures; in both lattices $Z=4$ and their Madelung constants differ by less than 0.2% (the first two shells of ions around a central ion are identical on the basis of pair interactions).

On the basis of the same model, the values of p can be determined from experimental data on compressibility of the solids, so that direct comparison with observed stability is possible. For crystals of the alkali halides the sodium-chloride ($B1$) configuration is predicted to be the most stable one for the allowed values of p. This agrees with experimental observation except for cesium chloride, bromide, and iodide, which exhibit $B2$ configuration at normal pressures and temperatures. Many efforts have been undertaken, on the basis of the Born-Mayer theory of ionic crystals, to explain

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* On leave of absence from the Institute of Industrial Chemistry, Polytechnic Institute, Milano, Italy.

[1] F. Hund, Z. Physik 34, 833 (1925).

[2] J. E. Lennard-Jones and A. E. Ingham, Proc. Roy. Soc. (London) A107, 636 (1925).

the $B2$ stability of these cesium salts, but these efforts have not been successful. A general conclusion is that the Born-Mayer model overestimates the stability of the $B1$ configuration by as much as a few kcal/mole for the heavier alkali halides. For a detailed review of such calculations, we refer to the excellent treatises by Born and Huang,[3] Pauling,[4] and Seitz.[5] Recently, an extensive survey concerning the cohesive energies of ionic solids in the Born-Mayer model was given by Tosi.[6] Similar difficulties were encountered by Mayer[7,8] in an attempt to explain the observed $B3$, $B4$ stability of the halides of silver and monovalent copper, as well as the $B2$ stability of monovalent thallium halides. We note that in these cases, the cations are *not* isoelectronic with rare-gas atoms.

In going to crystals of RX compounds of the types II-VI and III-V, the difficulties regarding stability on the basis of the Born-Mayer theory become more pronounced. Although the complication concerning the $B2$ configuration does not occur since this structure is not observed, several of the II-VI and III-V compounds crystallize in the $B3$ or $B4$ structure. The occurrence of these structures necessitates small values of the repulsion exponent p which are not allowed or unlikely on the basis of available data. In addition, the relative stability of the $B3$ and $B4$ lattices cannot be explained on this basis, since in this case the difference in lattice energy depends solely on the difference in Madelung constants, which is extremely small.

A different approach to crystal stability of ionic compounds is based on vast experimental evidence that the ratio between the "size" of cation and anion plays an important role for stability. Empirical rules for predicting the stable crystal structure of ionic (and other) solids from a knowledge of ionic (or atomic) radii alone were formulated by Goldschmidt.[9] The effect of ionic size can be taken into account most explicitly on the basis of a model of rigid spheres with point-charge interactions only; the parameters are then Z, M, and the ratio (r_+/r_-) between the sizes of cation and anion.

Also this model of rigid spheres is deficient in several respects, but it strikingly confirms experimental evidence that coordination number $Z=4$ is associated with small values of r_+/r_- (e.g., silver iodide). This rule appears not to hold for the alkali halides; e.g., sodium iodide has $B1$ structure. In any case, such model calculations show that the ratio of ionic sizes is indeed an important parameter in determining the stable crystal structure.

The difficulties associated with the Born-Mayer theory, in particular with reference to the $B3$ and $B4$ structures, have led to the assumption that the occurrence of the $B3$ and $B4$ configurations implies an essential deviation from an ionic description of the corresponding RX compounds. This assumption appeared the more reasonable since it was observed that typically "covalent" crystals of elements in the fourth column of the periodic table exhibit exclusively (with the exception of graphite) structures with coordination number $Z=4$. The diamond arrangement, identical with the sphalerite structure for $R=X$, is shown by C, Si, Ge, and Sn. Also SiC has the sphalerite configuration. Another factor in favor of the viewpoint that covalency plays a role for the lattice energies of compounds with $B3$, $B4$ structures lies in the observation that the calculated energies[7,8,10] with the Born-Mayer model for the silver, thallium, and (monovalent) copper halides are considerably less negative than the experimental values. These discrepancies, which are largest for the salts which crystallize in the $B3$, $B4$ structures (copper halides and silver iodide), point to an additional source of attractive energy between the ions.

Especially the pioneering work by Pauling and coworkers[4] resulted in a general acceptance of the covalent and "mixed" covalent-ionic types of binding in crystals of RX compounds.[11] The adoption of these concepts has led to a description and classification of many phenomena concerning molecules and solids which is self-consistent at least from a qualitative or semiquantitative point of view.

On the other hand, the mathematical difficulties associated with the accurate theoretical evaluation of covalent or homopolar bonding in molecules or solids are so formidable, even for the simplest systems, that a quantitative comparison with experiments cannot be made. Also, estimates of the degree of ionicity of one and the same solid have given widely different results, depending upon the type of experimental phenomenon analyzed. A critical comparison between the "covalent" and "ionic" models was undertaken by Folberth,[12] from which he concluded that the ionicity of bonding for compounds with $B3$, $B4$ structures is considerably larger than is usually assumed. Obviously, the covalency concept does not enable us to interpret the relative stability of the $B3$ and $B4$ structures, nor does it contribute to the stability problem of the $B2$-configuration for cesium halides.

In this paper, we will present an explanation of crystal stability for II-VI and III-V compounds which is a straightforward extension of the theory developed earlier for the stability of rare-gas crystals[13] and of the

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[3] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954), Chaps. I and III.

[4] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), Chap. 13.

[5] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. 2.

[6] M. P. Tosi, Solid State Phys. **16**, 1 (1964).

[7] J. E. Mayer, J. Chem. Phys. **1**, 327 (1933).

[8] J. E. Mayer and R. B. Levy, J. Chem. Phys. **1**, 647 (1933).

[9] V. M. Goldschmidt, Fortschr. Mineral. **15**, 73 (1931).

[10] M. F. C. Ladd and W. H. Lee, Trans. Faraday Soc. **54**, 34 (1958).

[11] See, e.g., R. C. Evans, *An Introduction to Crystal Chemistry* (Cambridge University Press, New York, 1952).

[12] O. G. Folberth, Z. Naturforsch. **15a**, 425 (1960).

[13] L. Jansen, Phys. Rev. **135**, A1292 (1964), hereafter referred to as I.

solid alkali halides.[14] We have shown that the stability of the face-centered cubic configuration for solid neon, argon, krypton, and xenon, which cannot be explained on the basis of a pair potential between the atoms, is due to the effect of simultaneous exchange interactions between three rare-gas atoms in first and second orders of perturbation theory.[13] On a similar basis we have shown that the $B2$ stability of cesium halides and the observed transition pressures for potassium and rubidium halides are explained on the basis of simultaneous exchange interactions between three ions.[14] The main aspects of these stability analyses are summarized in the next Section.

The theory will now be extended to include also crystals of II-VI and III-V compounds. One limitation must be made at the outset: We consider only those elements of the second and third columns of the periodic table whose ions are *isoelectronic* with rare-gas atoms. This includes Be, Mg, Ca, Sr, Ba and B, Al, Sc, Y, La as cations. For the present we exclude ions which have complete $3d$, $4d$, and $5d$ shells, i.e., those of Zn, Cd, Hg, as well as Ga, In, and (trivalent) Tl.

SUMMARY OF THREE-ATOM AND THREE-ION INTERACTIONS

We will first summarize the main aspects of the stability analyses developed in I and II for rare-gas crystals and solid alkali halides, respectively; the same methods will be used for the analysis of crystal stability of II-VI and III-V compounds.

For *rare-gas crystals* the problem concerns the observed stability of the face-centered cubic (fcc) configuration for solid neon, argon, krypton, and xenon; a pair potential calculation of the static lattice energy predicts the hexagonal close-packed (hcp) structure to be slightly more stable. For *alkali-halide crystals*, as mentioned before, pair interactions give consistently a more negative lattice energy of the sodium chloride ($B1$) arrangement of ions for all halides. The observed occurrence of unexplained structures is in both cases characteristic for a number of representatives of the series. This indicates that crystal stability is not sensitively dependent upon the precise analytic form of the wave functions for the atoms or ions, but that it is determined by more general parameters characterizing the charge distributions, relative size of the ions, etc.

A detailed analysis leads in both cases to the expectation that the omission of simultaneous interactions between more than two atoms or ions is the principal cause of the discrepancies between theory and experiment. We consider only *three*-atom and *three*-ion interactions; if simultaneous interactions involving still larger numbers of particles are significant, a "molecular" description of these solids breaks down, contrary to experimental evidence. The three-body interactions must be of short range, i.e., of exchange type, and relatively strong, since for alkali-halide crystals we have to overcome as much as a few kcal/mole of pair energy in favor of the $B1$ configuration.

Explicit calculations for neon atoms[15] showed that, up to the density of the crystal, only exchange of one pair of electrons between the same pair of atoms contributes significantly to the three-atom crystal energy. It has been verified (II) that the same holds for the *relative* three-ion energy (relative to the two-body component) for alkali-halide crystals, where the nearest-neighbor distance is considerably smaller than for rare-gas solids because of electrostatic compression.

This *single-exchange* approximation makes it possible to use an average, or effective, electron density for the atoms or ions, which is chosen to be of Gaussian form.

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

where r is the distance between the effective electron and its nucleus, and where β is a parameter which can be determined from experiment. It should be noted that the stability results are not a sensitive function of the Gaussian parameter β. For a given structure, the relative three-atom component of the crystal energy is a function only of the dimensionless quantity βR, where R is the nearest-neighbor distance.

In the case of ionic solids we have two different Gaussian parameters, β and β', one for the cation and the other for the anion of each compound. It is found that here the relative three-ion crystal energy, for a given structure, is a function only of βR and of a parameter γ, defined as

$$\gamma=(\beta'/\beta)^2\,,\quad \beta'>\beta\,. \qquad (2)$$

The parameter β' characterizes the smaller ion, β the larger ion of the pair RX. Usually, therefore, β' is associated with the cation and β with the anion of the pair. The values of β for rare-gas atoms are determined from pair-potential functions,[15] whereas for the ions an estimate is based on experimental values for the diamagnetic susceptibility, relative to rare-gas atoms (II).

Consider now a triplet (abc) of ions with one effective electron per ion, counterbalanced by nuclear charges of plus one. We assume that the essential effect of net ionic charges on crystal stability is reflected by the value of the Madelung constant, so that for the three-ion interactions the ions may be considered as electrically neutral.

The zero-order wave function is (Slater determinant)

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

where 1, 2, 3 number the electrons. The wave function

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[14] E. Lombardi and L. Jansen, Phys. Rev. **136**, A1011 (1964), hereafter referred to as II.

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

TABLE I. Values for Gaussian parameters β, in units 10^8 cm^{-1}, for ions of I-VII, II-VI, and III-V compounds, and compared with those of rare-gas atoms.

		N^{3-}	0.500	P^{3-}	0.400	As^{3-}	0.365	Sb^{3-}	0.320
		O^{2-}	0.600	S^{2-}	0.445	Se^{2-}	0.406	Te^{2-}	0.356
		F^-	0.936	Cl^-	0.558	Br^-	0.479	I^-	0.419
He	1.59	Ne	1.070	A	0.623	Kr	0.532	Xe	0.454
Li^+	2.60	Na^+	1.162	K^+	0.718	Rb^+	0.600	Cs^+	0.503
Be^{2+}	3.44	Mg^{2+}	1.384	Ca^{2+}	0.839	Sr^{2+}	0.663	Ba^{2+}	0.550
B^{3+}	4.86	Al^{3+}	2.030	Sc^{3+}	1.120	Y^{3+}	0.812	La^{3+}	0.666

for ion a is given by

$$\varphi_a(r)=\rho_a^{1/2}(r)=(\beta_a/\pi^{1/2})^{3/2}\exp(-\beta_a^2r_a^2/2)\,,\quad\cdots,\tag{4}$$

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

$$\Delta_{abc}^2=\Delta_{ab}^2+\Delta_{ac}^2+\Delta_{bc}^2-2\Delta_{ab}\Delta_{ac}\Delta_{bc}\tag{5}$$

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.

Let E_1 and E_2 denote the first- and second-order perturbation energies for the triplet (abc), and let $E_1^{(0)}$ and $E_2^{(0)}$ denote the total of first- and second-order pair energies, respectively. We determine the relative first- and second-order three-ion energies, i.e.,

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

and

$$\Delta E_2/E_2^{(0)}\equiv(E_2-E_2^{(0)})/E_2^{(0)}\tag{6}$$

as a function of the dimensions of each triangle (abc).

Since the three-atom and three-ion interactions are of exchange type and, therefore, of short range, it is sufficient to consider only triangles of small dimensions in each solid.

Explicit calculations were carried out for triplets of rare-gas atoms formed by a central atom and two of its nearest neighbors in the solid. Let β be the atomic Gaussian parameter, R the nearest-neighbor distance, and θ the opening of the isosceles triangle at the central atom. The relative three-atom interactions $\Delta E_1/E_1^{(0)}$ and $\Delta E_2/E_2^{(0)}$ are then functions only of βR and of θ.

TABLE II. Values for the dimensionless parameters βR and $\gamma=(\beta'/\beta)^2$ for crystals of the II-VI compounds; R denotes the nearest-neighbor distance and β represents the larger ion.

	O		S		Se		Te	
	βR	γ	βR	γ	βR	γ	βR	γ
Be	0.990	30.07	0.934	54.70	0.893	65.70	0.858	85.40
Mg	1.260	5.33	1.155	9.70	1.104	11.64	0.983	15.14
Ca	1.440	1.93	1.260	3.51	1.202	4.22	1.129	5.49
Sr	1.524	1.22	1.335	2.23	1.263	2.67	1.185	3.48
Ba	1.650	1.18	1.415	1.54	1.344	1.86	1.246	2.41

It was found that to a good approximation

$$\Delta E_1/E_1^{(0)}\approx\Delta E_2/E_2^{(0)}\,,\tag{7}$$

for all values of the opening θ. For the *total* relative three-atom interaction of each triangle, we may then write

$$\frac{\Delta E}{E^{(0)}}\equiv\frac{\Delta E_1+\Delta E_2}{E_1^{(0)}+E_2^{(0)}}\approx\frac{\Delta E_1}{E_1^{(0)}}\approx\frac{\Delta E_2}{E_2^{(0)}}\,.\tag{8}$$

The behavior of $\Delta E/E^{(0)}$, as a function of θ, is as follows (for details, we refer to I). The relative three-atom energy amounts to about -20% at $\theta=60°$ (equilateral triangle), increases rapidly and practically linearly with θ until $\theta\sim120°$, after which the curve flattens and becomes practically independent of θ. The value at $\theta=180°$ (linear symmetric array of atoms) is positive and considerably smaller in magnetitude than at $\theta=60°$ for the rare-gas crystals (βR between 2.0 and 3.4). Upon decreasing βR, the value of $\Delta E/E^{(0)}$ at $\theta=180^0$ increases, whereas the value at $\theta=60°$ remains approximately constant for βR between 1 and 2.

TABLE III. Values for the dimensionless parameters βR and $\gamma=(\beta'/\beta)^2$ for crystals of the III-V compounds: R denotes the nearest-neighbor distance and β represents the larger ion.

	N		P		As		Sb	
	βR	γ	βR	γ	βR	γ	βR	γ
B	0.782	94.65	0.786	148	0.755	177.60	[a]	231
Al	0.934	16.48	0.944	25.75	0.891	30.90	0.832	40.24
Sc	1.110	5.02	[a]	7.84	1.001	9.42	0.937	12.25
Y	1.219	2.64	[a]	4.12	1.056	4.95	[a]	6.44
La	1.326	1.78	1.203	2.78	1.118	3.33	1.036	4.34

[a] Structure unknown.

In going to ionic solids, the additional parameter determining the three-ion interactions is $\gamma=(\beta'/\beta)^2\geqslant1$. For values of γ between 1 and 2, it was found in II that the general properties of $\Delta E_1/E_1^{(0)}$, as a function of βR and θ, are very similar to those observed with rare-gas atoms. If $\gamma\gg1$, then the three-ion interactions for triplets $(\beta'\beta\beta)$ and $(\beta\beta'\beta')$ are considerably quenched and lose their structure sensitivity with respect to θ. In this case the main contribution to the three-ion lattice energy arises from triplets of the *large ions only.* This result will prove to be of importance in the analysis of the $B3$, $B4$ crystal stability for II-VI and III-V compounds, since the occurrence of these structures is always associated with large values of γ.

DETERMINATION OF GAUSSIAN PARAMETERS FOR II-VI AND III-V COMPOUNDS

The values of the Gaussian parameters β, β' for the ions of II-VI and III-V compounds have, as in the case of alkali halides, been determined from experimental values of the diamagnetic susceptibility, taking as a reference for each ion the corresponding isoelectronic rare-gas atom. Experimental values of diamagnetic susceptibilities are available[16,17] for all cations and for the anions of the sixth column. It appears that the β values for these anions are approximately 10% lower than those for the corresponding isoelectronic halide ions. We have, therefore, taken the β values for ions of the fifth column as again 10% lower than those of column six. In Table I we have collected the β values for rare-gas atoms and for ions of the alkali halides and of II-VI and III-V compounds.

In addition, we give in Tables II and III values of $\gamma = (\beta'/\beta)^2$ and of βR for the II-VI and III-V compounds; R denotes the nearest-neighbor distance in the lattice (from Wyckoff[18]) and β represents the larger ion.

The values in the last two tables should be viewed primarily in relation to each other and to those for rare-gas and alkali-halide crystals (compare Table 2 of II). For the rare-gas crystals, the values of βR lie between 2.0 (xenon) and 3.4 (neon); for the alkali-halide crystals they range from 1.26 (LiI) to 2.16 (NaF).

TABLE IV. Observed structures of the crystals of II-VI compounds (ions isoelectronic with rare-gas atoms). Data taken from Wyckoff (Ref. 18).

	O	S	Se	Te
Be	*B*4	*B*3	*B*3	*B*3
Mg	*B*1	*B*1	*B*1	*B*4
Ca	*B*1	*B*1	*B*1	*B*1
Sr	*B*1	*B*1	*B*1	*B*1
Ba	*B*1	*B*1	*B*1	*B*1

ANALYSIS OF CRYSTAL STRUCTURES OF II-VI AND III-V COMPOUNDS

The observed crystal structures of II-VI and III-V compounds whose ions are isoelectronic with rare-gas atoms are given in Tables IV and V, respectively; the data were taken from Wyckoff.[18]

These data refer to standard conditions. Concerning polymorphisms, we remark that BN has also been observed in two graphite-like structures under standard conditions.[18] It is of particular importance to observe that polymorphism under pressure has *not* been found for the II-VI and III-V compounds whose ions are isoelectronic with rare-gas atoms.[19] On the other hand, pressure transitions are a *very common* phenomenon for those II-VI and III-V compounds whose cations have closed $3d$, $4d$, or $5d$ shells.[19]

It is seen, from a comparison with Table II, that the *B*3, *B*4 structures only occur in association with *large* values of γ and the *smallest* values of βR. As we mentioned before, the determination of three-ion interactions is simple in this case, since we have to consider only triplets of anions, which exhibit rare-gas crystal structures both in the *B*3 and the *B*4 configurations.

TABLE V. Observed structures of the crystals of III-V compounds (ions isoelectronic with rare-gas atoms). Data taken from Wyckoff (Ref. 18).

	N	P	As	Sb
B	*B*3	*B*3	*B*3	a
Al	*B*4	*B*3	*B*3	*B*3
Sc	*B*1	a	*B*1	*B*1
Y	*B*1	a	*B*1	a
La	*B*1	*B*1	*B*1	*B*1

[a] Structure unknown.

For the evaluation of the total three-ion crystal energy $E\{3\}$ we must determine all possible triplet configurations involving a central ion and two ions of the first few neighboring shells in the four structures *B*1, *B*2, *B*3, and *B*4. As for the alkali-halide crystals, we denote a cation by C and an anion by A and add subscripts 1, 2, $\cdots$ to distinguish between different shells around the central ion. The subscript zero refers to the central anion or cation. In Tables VI–X all triangles are listed which are of possible importance for the evaluation of the three-ion energies in the four structures. Table VI refers to triplets $A_0C_1C_1$ (or $C_0A_1A_1$), i.e., to those with a central anion (cation) and two nearest-neighbor cations (anions). Further mixed cation-anion triangles are of no importance in crystals of II-VI and III-V compounds. Consequently, Tables VII–X refer to (isosceles) triangles of anions *only*. We denote such triangles by $A_0A_nA_n$, where n now numbers the *anion shells* (1, 2, $\cdots$).

THREE-ION ENERGIES FOR CRYSTALS OF II-VI AND III-V COMPOUNDS

Formalism

We now discuss the evaluation of three-ion contributions to the lattice energies of II-VI and III-V compounds, following the theory developed in I and II for rare-gas and alkali-halide crystals. As a simplifi-

TABLE VI. Number of pairs and triplets involving a central ion and its first shell of neighbors, for the *B*1, *B*2, *B*3, and *B*4 structures. The opening of the triangle at the central ion is denoted by θ.

Structure	Number of pairs	Number of triplets $A_0C_1C_1$, $C_0A_1A_1$	$\cos\theta$
*B*1	6	12	0.0000
		3	−1.0000
*B*2	8	12	+0.3333
		12	−0.3333
		4	−1.0000
*B*3	4	6	−0.3333
*B*4	4	6	−0.3333

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[16] C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1957), Chap. 9.

[17] Landolt-Bornstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1950), Vol. I, p. 396.

[18] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, New York, 1963), Chap. III.

[19] A. Jayaraman, W. Klement, and G. C. Kennedy, Phys. Rev. **130**, 2277 (1963) (a complete list of other references is found in this paper).

TABLE VII. Analysis of the $B1$ (sodium chloride) structure in terms of numbers of anions and of isosceles triangles of the type $A_0A_nA_n$, for the first few values of n. The opening of the triangle $A_0A_nA_n$ at the central anion is denoted by θ. R is the nearest-neighbor (anion-cation) distance in the lattice.

n	Number of anions	Distance from center in units of R	Number of triplets	$\cos\theta$
1	12	$2^{1/2}$	8	+0.5000
			12	0.0000
			24	−0.5000
			6	−1.0000
2	6	2	12	0.0000
			3	−1.0000
3	24	$6^{1/2}$	24	+0.8333
			24	+0.6666
			8	+0.5000
			12	+0.3333
			48	+0.1666
			48	−0.1666
			12	−0.3333
			24	−0.5000
			24	−0.6666
			24	−0.8333
			12	−1.0000
4	12	$8^{1/2}$	as $A_0A_1A_1$	
5	24	$10^{1/2}$	24	+0.9000
			12	+0.8000
			12	+0.6000
			48	+0.3000
			24	+0.1000
			24	0.0000
			24	−0.1000
			48	−0.3000
			12	−0.6000
			12	−0.8000
			24	−0.9000
			12	−1.0000
6	8	$12^{1/2}$	12	+0.3333
			12	−0.3333
			4	−1.0000

cation, we limit ourselves to the absolute zero of temperature and neglect the effect of zero-point energy on stability, so that we must compare only the *static* lattice energies of the four different configurations for these compounds.

It will be shown how a consistent explanation of the observed stability relations can be given *on the basis of a Born-Mayer model for ionic solids plus three-ion interactions in first and second orders of perturbation theory.* As mentioned before, cation and anion are considered as electrically *neutral* for the evaluation of the three-ion energy, i.e., we assume that the effect of purely electrostatic forces on crystal stability is essentially reflected by the different values of the Madelung constant of the four structures considered. For convenience, we will nevertheless speak of ion, cation, and anion, also in connection with the three-body energy of the lattices.

The evaluation of three-ion energies closely follows that of Ref. 14. The static lattice energy of N anions and N cations, with fixed positions r_1, r_2, $\cdots$, r_N, is written as a series of terms depending upon the coordinates of increasing numbers of ions, as follows

$$E(r_1,r_2,\cdots,r_N)=E\{2\}+E\{3\}+E\{4\}+\cdots, \quad (9)$$

where $E\{2\}$ contains all pair interactions, $E\{3\}$ all triplet interactions, etc. We assume that the series converges rapidly for molecular and ionic solids and that it may be terminated with $E\{3\}$.

Denoting an arbitrary triplet of ions by (abc), then $E\{3\}$ is the limiting value of $E-E\{2\}$ if all simultaneous interactions between more than three ions are discarded, i.e.,

$$\begin{aligned} E\{3\} &= \sum_{a<b<c} [E(abc)-\{E^{(0)}(ab)+E^{(0)}(ac) \\ &\qquad\qquad +E^{(0)}(bc)\}] \\ &\equiv \sum_{a<b<c} \Delta E(abc), \end{aligned} \quad (10)$$

where $E(abc)$ denotes the total energy of interaction (first- plus second-order) for the *isolated* triplet (abc) and $E^{(0)}(ab)$ the interaction for the *isolated* pair (ab); the summation extends over all possible triplets. We write $E^{(0)}=E_1^{(0)}+E_2^{(0)}$ and $\Delta E=\Delta E_1+\Delta E_2$ for an arbitrary triplet of ions, as before.

First, we consider the *pair energy* $E\{2\}$ of the crystal. As in the case of alkali-halide crystals accurate expressions for the pair interactions between ions of the II-VI and III-V compounds are not known. However, since we have assumed that the *relative* stability of the different solid phases is determined primarily by *three-*

TABLE VIII. Analysis of the $B2$ (cesium chloride) structure in terms of numbers of anions and of isosceles triangles of the type $A_0A_nA_n$, for the first few values of n. The opening of the triangle $A_0A_nA_n$ at the central anion is denoted by θ. R is the nearest-neighbor (anion-cation) distance in the lattice.

n	Number of anions	Distance from center in units of R	Number of triplets	$\cos\theta$
1	6	$(4/3)^{1/2}$	as $A_0A_2A_2$ of $B1$	
2	12	$(8/3)^{1/2}$	as $A_0A_1A_1$ of $B1$	
3	8	2	as $A_0A_6A_6$ of $B1$	
4	6	$(16/3)^{1/2}$	as $A_0A_2A_2$ of $B1$	
5	24	$(20/3)^{1/2}$	36	+0.8000
			12	+0.6000
			48	+0.4000
			24	+0.2000
			24	0.0000
			24	−0.2000
			48	−0.4000
			12	−0.6000
			36	−0.8000
			12	−1.0000
6	24	$8^{1/2}$	as $A_0A_3A_3$ of $B1$	
7	12	$(32/3)^{1/2}$	as $A_0A_1A_1$ of $B1$	
8	30	$(12)^{1/2}$	24	+0.8888
			12	+0.7777
			48	+0.6666
			48	+0.4444
			24	+0.3333
			24	+0.1111
			60	0.0000
			24	−0.1111
			24	−0.3333
			48	−0.4444
			48	−0.6666
			12	−0.7777
			24	−0.8888
			15	−1.0000
9	24	$(40/3)^{1/2}$	as $A_0A_5A_5$ of $B1$	

ion interactions, the precise analytical form of the pair potential is not of importance. Consequently, we can choose the pair potential in such a way that it ensures stability of each solid phase separately. Following the analysis for alkali-halide crystals, we use for the pair interactions a model of electrostatic forces between point charges, supplemented by repulsion between the closed shells of different ions. As in II, the pair repulsions are identified with the *first*-order interactions between a pair of ions. It should be noted that, if the ions are very close together (smallest values of βR) also the *second*-order interactions contribute to the pair repulsion between the ions. Neglecting this difference for the moment, we write the total pair energy $E\{2\}$ for each II-VI and III-V compound and in each structure considered, as a sum of Madelung energy E_M and of the total first-order repulsion between the ions, i.e., as

$$E\{2\}=E_M+\sum_{a<b} E_1^{(0)}(ab). \qquad (11)$$

In each structure, a central anion (cation) is surrounded by a first shell of cations (anions), followed by a second shell of anions (cations); etc. Let, for a given structure and for given lattice parameters, α_1 denote the repulsion of the pair A_0C_1, i.e., that between a central anion and a nearest-neighbor cation. The only remaining repulsions to be considered for II-VI and III-V compounds are those for pairs A_0A_n of anions, for the first few values of n; this repulsion is denoted by α_n. We equate the ratios α_n/α_1 to the corresponding ratios of first-order interactions between Gaussian ions. In this way we can, for given values of γ, βR and for each structure, express $E\{2\}$ as a function of the Madelung energy and the repulsion α_1 for a nearest-neighbor pair of ions.

TABLE IX. Analysis of the $B3$ (sphalerite) structure in terms of numbers of anions and of isosceles triangles of the type $A_0A_nA_n$, for the first few values of n. The opening of the triangle $A_0A_nA_n$ at the central anion is denoted by θ. R is the nearest-neighbor (anion-cation) distance in the lattice.

n	Number of anions	Distance from center in units of R	Number of triplets	$\cos\theta$
1	12	$(8/3)^{1/2}$	as $A_0A_1A_1$ of $B1$	
2	6	$(16/3)^{1/2}$	as $A_0A_2A_2$ of $B1$	
3	24	$8^{1/2}$	as $A_0A_3A_3$ of $B1$	
4	12	$(32/3)^{1/2}$	as $A_0A_4A_4$ of $B1$	
5	24	$(40/3)^{1/2}$	as $A_0A_5A_5$ of $B1$	

Next, we consider the *three-ion* crystal energy $E\{3\}$. Let, as before, $\Delta E=\Delta E_1+\Delta E_2$ denote the three-ion interaction for an arbitrary triplet and $\Delta E_1/E_1^{(0)}$, $\Delta E_2/E_2^{(0)}$ the relative first- and second-order three-ion interactions. As for alkali-halide crystals we assume $\Delta E_1/E_1^{(0)}\approx\Delta E_2/E_2^{(0)}$, which approximation is justified in the two limits $\gamma\sim1$ and $\gamma\gg1$. It is noted that the case $\gamma\gg1$ always applies for those II-VI and III-V compounds which crystallize in the $B3$ or $B4$ structure.

With the above assumption one may write, following (8), for an arbitrary triplet (abc) of ions

$$\Delta E=\Delta E_1+\Delta E_2\approx(\Delta E_1/E_1^{(0)}) \times E_1^{(0)}(1+E_2^{(0)}/E_1^{(0)}), \qquad (12)$$

with

$$E_1^{(0)}=E_1^{(0)}(ab)+E_1^{(0)}(ac)+E_1^{(0)}(bc),$$

TABLE X. Analysis of the $B4$ (wurtzite) structure in terms of numbers of anions and of isosceles triangles of the type $A_0A_nA_n$, for the first few values of n. The opening of the triangle $A_0A_nA_n$ at the central anion is denoted by θ. R is the nearest-neighbor (anion-cation) distance in the lattice.

n	Number of anions	Distance from center in units of R	Number of triplets	$\cos\theta$	Number of triplets	$\cos\theta$
1	12	$(8/3)^{1/2}$	8	+0.5000	18	−0.5000
			12	0.0000	6	−0.8333
			3	−0.3333	3	−1.0000
2	6	$(16/3)^{1/2}$	3	+0.3333		
			6	0.0000		
			6	−0.6666		
3	2	8/3	1	−1.0000		
4	18	$8^{1/2}$	18	+0.8333	24	−0.1666
			12	+0.6666	12	−0.5000
			6	+0.5555	12	−0.6111
			2	+0.5000	12	−0.6666
			6	+0.3888	12	−0.8333
			6	+0.3333	6	−0.9444
			12	+0.1666	3	−1.0000
			6	−0.1111		
5	12	$(88/9)^{1/2}$	12	+0.8636	12	−0.5909
			12	+0.5909	12	−0.8636
			6	+0.4545	6	−1.0000
			6	−0.4545		
6	6	$(32/3)^{1/2}$	2	+0.5000		
			6	−0.5000		
			3	−1.0000		
7	12	$(40/3)^{1/2}$	6	+0.9000	12	−0.3000
			6	+0.7333	12	−0.5666
			6	+0.6333	6	−0.6000
			6	+0.1000	6	−0.8666
			6	−0.1666		

the sum of interactions for the isolated pairs of the triplet. If the values of βR are so small that also second-order interactions contribute to the pair repulsion, then we must replace $E_1^{(0)}(ab)$ in (11) by the sum, $E_{\mathrm{rep}}^{(0)}(ab)$, of $E_1^{(0)}(ab)$ and the repulsive component of $E_2^{(0)}(ab)$. Since the pair interaction $E^{(0)}$ for each triplet can be written as $E^{(0)}=E_1^{(0)}+E_2^{(0)}=E_{\mathrm{rep}}^{(0)}+E_{\mathrm{attr}}^{(0)}$, where $E_{\mathrm{attr}}^{(0)}$ denotes the total pair attraction for the triplet, (12) can be written as

$$\begin{aligned}\Delta E&\approx(\Delta E_1/E_1^{(0)})E_1^{(0)}(1+E_2^{(0)}/E_1^{(0)})\\&=(\Delta E_1/E_1^{(0)})E_{\mathrm{rep}}^{(0)}(1+E_{\mathrm{attr}}^{(0)}/E_{\mathrm{rep}}^{(0)}).\qquad(12')\end{aligned}$$

For any given triplet of ions $E_1^{(0)}$ (or $E_{\mathrm{rep}}^{(0)}$) can be expressed in terms of α_1, the repulsion for a pair of nearest-neighbor ions. It follows from (12, 12′) that for each triplet the three-ion energy is a function of α_1, of the relative first-order three-ion interaction $\Delta E_1/E_1^{(0)}$, and *of the ratio between the attractive and repulsive components of the pair energy for the triplet.* It is important to note that in this case the attractive (van der Waals) pair interactions must explicitly be taken into account. The three-ion crystal energy $E\,\{3\}$ is the sum of (12′) over all triplets of ions.

In the *next step* of the stability analysis we sum $E\,\{2\}$ and $E\,\{3\}$, as a function of α_1, for the four different structures. This sum, for the observed 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. For some of the II-VI and III-V compounds, the crystal energies have either not been determined, or they are not known with precision. In these cases we adopt a Born-Mayer model and write for the static lattice energy

$$E=E_M(1-1/p),\qquad(13)$$

where p is the exponent of the pair repulsion. The quantity α_1 is then determined for a *range* of values of p.

Finally, with the value(s) of α_1 obtained as described, we calculate the lattice energies of the other structures and compare these values to determine the relative stability of the $B1$, $B2$, $B3$, and $B4$ configurations for each compound.

THREE-ION INTERACTIONS AND CRYSTAL STABILITY

General Aspects

The main characteristics concerning the role of three-ion interactions in determining crystal stability for a given type of compound can be deduced from (12′). First, we consider the limiting case of $\gamma\sim1$, i.e., rare-gas atoms as well as alkali halides and II-VI, III-V compounds with the heaviest cations. We form all triplets consisting of a central ion and two ions from a given shell around it. For any model of pair interactions in which both the attractive and repulsive components are rapidly decreasing with distance, the ratio $E_{\mathrm{attr}}^{(0)}/E_{\mathrm{rep}}^{(0)}$ is practically the same, no matter which two ions are selected from the given shell. Consequently, we can characterize each *shell* by a certain value of $E_{\mathrm{attr}}^{(0)}/E_{\mathrm{rep}}^{(0)}$, determined by the distance between that shell and the central ion. Apparently, there are two possibilities:

(a) $|E_{\mathrm{attr}}^{(0)}/E_{\mathrm{rep}}^{(0)}|<1$, i.e., shell and central ion *repel* each other. In that case ΔE has the same sign as the relative first-order three-ion interaction $\Delta E_1/E_1^{(0)}$, which is negative for triangles with small opening, and positive for triangles with large opening at the central ion.

Consequently, the three-ion contributions favor the crystal structure *with the largest number of triangles of small opening*, each contribution weighted by the pair repulsion $E_1^{(0)}$.

(b) $|E_{\mathrm{attr}}^{(0)}/E_{\mathrm{iep}}^{(0)}|>1$, i.e., shell and central ion *attract* each other. In this case the sign of ΔE is the opposite of that of $\Delta E_1/E_1^{(0)}$. Consequently, such three-ion interactions (weighted by a factor $E_1^{(0)}$) favor the crystal structure *with the largest number of triangles of large opening.* The total three-ion energy $E\,\{3\}$ is the sum of contributions from the different shells. The number of shells to be taken into account is in any case small; ΔE per shell decreases with increasing distance in approximately the same way as the repulsive interaction between shell and central ion.

It is seen that the ratio $E_{\mathrm{attr}}^{(0)}/E_{\mathrm{rep}}^{(0)}$ for each shell plays an important role in determining the most stable crystal structure for a given compound. Some insight regarding the contributions from different shells can be obtained by considering the isoelectronic series rare-gas atoms, alkali halides, II-VI and III-V compounds with elements from the principal columns of the periodic table.

Rare-Gas Crystals. These solids are associated with the largest values of βR, as there is no Madelung energy to compress the crystals. In that case, only the shell of nearest neighbors around a central atom plays a role for three-atom interactions. Since, except for solid helium, nearest neighbors are situated approximately at the distance of minimum pair potential, we may take $|E_{\mathrm{attr}}^{(0)}/E_{\mathrm{rep}}^{(0)}|\approx2$ [$p/(p-6)$ for a Lennard-Jones $(p,6)$ potential; $p=12$ is a good approximation]. Consequently, case (b) above applies; the stable crystal structure is the one with the maximum number of triangles of large opening, which is the face-centered cubic configuration. (For details, we refer to I.)

Alkali-Halide Crystals. Owing to compression by the Madelung energy, the βR values for alkali-halide crystals are considerably smaller than those for the solid rare gases. For alkali halides with γ not much different from one, they lie between 1.65 and 1.85 (cf. Table 3 of II). The *first* shell of cations (anions) and a central anion (cation) now *repel* each other in the $B1$

(sodium chloride) and $B2$ (cesium chloride) configurations. We have, in II, estimated $|E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}|$ for the first shell, on the basis of a Lennard-Jones potential, to vary between 0.4 and 0.6; stability does not depend sensitively on the precise values of the ratio within this range.

The βR values for the *second* shell of ions lie in the range of those for heavy rare-gas crystals; consequently, we have taken a ratio $|E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}|=2$ for three-ion contributions from the second shell. It was found that contributions to ΔE from the first shell are always *attractive* and that they favor the $B2$ configuration; contributions from the second shell are always ***repulsive*** and favor the $B1$ configuration. The stability of the $B2$ structure for CsCl, CsBr, and CsI arises from the fact that the three-ion contributions from the first shell dominate sufficiently to overcome the few kcal/mole difference in pair energy in favor of the $B1$ structure. (For details we refer to II.)

Crystals of II-VI and III-V Compounds. The electrostatic compression in these solids is very strong, so that a still larger number of shells around a central ion must be taken into account for the evaluation of the three-ion energy. The salts with the lowest γ values are CaO ($\gamma=1.44$), SrO($\gamma=1.52$), BaO($\gamma=1.65$), BaS($\gamma=1.42$), BaSe($\gamma=1.43$), and LaN($\gamma=1.78$); the βR values lie in the range between 1.25 and 1.56 (Tables II and III). All these compounds crystallize in the $B1$ configuration.

The observed stability of the $B1$ structure is, of course, ***in agreement*** with predictions from the Born-Mayer model, for values of the repulsion exponent p between 6.3 and 33. Consequently, already the pair energy $E\,\{2\}$ explains the observed structure. To study the effect of the three-ion energy $E\,\{3\}$, we start from larger values of βR, i.e., from alkali-halide crystals, and compress the solid. For large values of βR only the first shell of ions is in the repulsive field of the central ion; its contribution to $E\,\{3\}$ favors the $B2$ structure. The second shell of ions, in the attractive field of the central ion, favors the $B1$ configuration. Upon compression, first the second shell of the $B2$ structure will go into the repulsive field of the central ion (distance $(4/3)^{1/2}R$), followed by the second shell of the $B1$ lattice (distance $2^{1/2}R$) at higher compression. The contributions to $E\,\{3\}$ from the second shells now ***change sign***, i.e., also the second shells favor the $B2$ configuration. It appears, however, that this gain in energy of the $B2$ structure is overcompensated by contributions to $E\,\{3\}$ *from further shells*, giving rise to larger repulsive three-ion energy in $B2$ than in $B1$. The total effect is in favor of $B1$, ruling out the stability of the $B2$ structure at these small values of βR.

TABLE XI. Values of the ratio $|E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}|$ for two Gaussian atoms ($\gamma=1$) as a function of the parameter $\beta e^2/E_{\text{av}}$, where E_{av} is an average excitation energy for the atom. The values of βR lie between 0.8 and 1.6.

$\beta e^2/E_{\text{av}}$	$\beta R=0.8$	$\beta R=1$	$\beta R=1.2$	$\beta R=1.4$	$\beta R=1.6$
0.3	0.515	0.449	0.398	0.356	0.329
0.4	0.566	0.496	0.442	0.400	0.368
0.5	0.601	0.530	0.474	0.430	0.396
0.6	0.627	0.555	0.498	0.452	0.417
0.7	0.647	0.574	0.516	0.469	0.434
0.8	0.663	0.590	0.531	0.483	0.447
0.9	0.676	0.602	0.543	0.495	0.456
1.0	0.687	0.613	0.553	0.504	0.467

Some insight can also be obtained regarding the stability of the $B3$ and $B4$ structures. Both lattice types have coordination number $Z=4$; the second shell of ions is at the relatively large distance $(8/3)^{1/2}R$ from a central ion. There are 6 triangles $A_0C_1C_1$ (or $C_0A_1A_1$), each with the tetrahedral opening $\theta=109°\,28'$ at the central ion. We have found in I and II that the contribution to $E\,\{3\}$ from triangles with opening $\theta\sim110°$ is very small. Therefore, the first shell of ions gives a negligible contribution to $E\,\{3\}$ in the $B3$, $B4$ structures.

There are 12 second neighbors in the $B3$ and $B4$ structures, forming 66 isosceles triangles with the central (like) ion. Because of the relatively large distance between second shell and central ion, this shell remains in the attractive field of the central ion unless the solid is highly compressed. Like ions in the $B3$, $B4$ structures have fcc and hcp configurations, respectively. It follows, from I, that the contribution to $E\,\{3\}$ from the second shells is ***repulsive***, so that the stability of these configurations is still *less* than predicted on the basis of a Born-Mayer model. The observed stability of the $B3$, $B4$ structures must, therefore, be ascribed to contributions to $E\,\{3\}$ from *further* shells. Such shells become important only at the smallest values of βR, so that stability of $B3$ and $B4$ should occur only under high electrostatic compression.

To evaluate $E\,\{3\}$ for the different structures, we must estimate the ratio $|E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}|$ occurring in the expression (12′) for the three-ion energy of each triplet. Because of larger electrostatic compression the βR values for II-VI and III-V compounds are smaller than for alkali halides with comparable values of γ. Compare, e.g., SrO and CsCl: in the first case $\gamma=1.22$, $\beta R=1.52$, whereas in the second case $\gamma=1.23$, but $\beta R=1.79$. An estimate on the basis of a Lennard-Jones $(p,6)$-potential is too inaccurate, both at small and at large distances, in view of uncertainty concerning the value of p. For such a potential, $|E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}|=(R'/\sigma)^{p-6}$, where R' is the interionic distance and σ the distance for zero potential, so that the ratio varies very rapidly with varying p at small and at large distances. We have, therefore, calculated this ratio directly from the first- and second-order interaction energies between two Gaussian atoms ($\gamma=1$), applying Eq. (13) of Ref. 20 and Eq. (27) of I, limited to the pair (ab). Different values were chosen for the parameter $\beta e^2/E_{\text{av}}$, where E_{av} is an average excitation energy for

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[20] L. Jansen, Phys. Rev. **125**, 1798 (1962).

the atom. The results, for small distances, are given in Table XI.

We conclude from the table that the values of $|E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}|$ increase slowly with decreasing distance between the ions. It appears justified to use average value of 0.5 for this ratio at small distances, in agreement with the estimate in II for alkali-halide crystals, where the ratio was assumed to vary between 0.4 and 0.6. At large distances we may identify $E_1^{(0)}$ with $E_{\text{rep}}^{(0)}$ and $E_2^{(0)}$ with $E_{\text{attr}}^{(0)}$; it is found that the ratio $|E_2^{(0)}/E_1^{(0)}|$ increases slowly with increasing distance and that an average value of 2 is a good approximation. In the numerical analysis also larger values were used for further shells; this modification has little effect on stability.

For several II-VI and III-V compounds $\gamma \gg 1$, i.e., cation and anion differ considerably in size; these compounds are always associated with $B3$ or $B4$ stability. The βR values for these crystals are smaller than in the case of $\gamma \sim 1$, since the nearest-neighbor repulsion is now much smaller. Another consequence of $\gamma \gg 1$ is that the three-ion crystal energy $E\,\{3\}$ is determined essentially by triplets of *anions alone*. The evaluation of the three-ion crystal energy reduces in this case to a summation over triplets in a simple-cubic lattice for $B2$, a face-centered cubic lattice for $B1$ and $B3$, and a hexagonal close-packed structure for $B4$.

Finally, for a third category of II-VI and III-V compounds the γ values are neither close to one, nor are they very large; compounds with cations of Mg, Ca, and Sc, Y and La belong to this type. The associated βR values are also intermediate between those typical for $B1$ and those for $B3$, $B4$ stability. In these crystals there is some contribution to $E\,\{3\}$ from triplets involving cations; in addition, it is more difficult to give reliable estimates of the $|E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}|$ values. In the following numerical analysis several possible sets of values are used for this ratio in the different structures.

NUMERICAL RESULTS

We will now present the numerical results of the stability analysis for II-VI and III-V compounds, comparing the structures $B1$, $B2$, $B3$, and $B4$. Each solid is characterized by the Gaussian parameter $\gamma = (\beta'/\beta)^2$ and by βR, where β represents the larger ion of the compound (the anion in all cases) and where R is the nearest-neighbor distance in the stable configuration.

In the following Tables XII and XIII we list, for each compound in all four structures, first the Madelung energy in kcal/mole, followed by the total pair energy in units of the nearest-neighbor repulsion α_1. The remaining columns contain values for the total first-order three-ion energy , in units of α_1, *per shell* of ions around a central ion. First, we list the sum of ΔE_1 for nearest-neighbor triplets $A_0C_1C_1$ and $C_0A_1A_1$; the following columns, labeled 1–9, refer to the sum for triplets $A_0A_nA_n$ and $C_0C_nC_n$, for $n = 1, 2, \cdots, 9$. It may be remarked that the contributions to ΔE_1 from triplets $C_0C_nC_n$ are vanishingly small except for the smallest values of γ and intermediate values of βR (e.g., ScN, LaP), where they are at most of the order of 1% of the contributions from corresponding triplets $A_0A_nA_n$. For $n > 2$ the contributions from cation triplets are always zero.

To obtain the total (first- plus second-order) three-ion energy for each shell and in each structure, we must multiply the values of the tables by the factor $(1 + E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)})$, where $E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ is averaged over all triplets formed by a central ion and two ions from that shell of ions.

For the discussion of relative stability of the four structures it is of advantage to distinguish between the following three categories of solids:

(A) *βR large and γ small*, i.e., $\beta R \geqslant 1.2$; $\gamma \leqslant 6$. To this category belong: MgO, CaO, SrO, BaO; CaS, SrS, BaS; CaSe, SrSe, BaSe; SrTe, BaTe; YN, LaN, and LaP;

(B) *βR small and γ large*, i.e., $\beta R \leqslant 1.0$; $\gamma \geqslant 10$. The following salts belong to this category: BeO, BeS, BeSe, BeTe; MgTe; BN, BP, BAs; AlN, AlP, AlAs, and AlSb;

(C) *βR and γ intermediate*, i.e., $1.0 \leqslant \beta R \leqslant 1.2$ and γ between 3 and 10 approximately. The salts which belong to this third category are: MgS, MgSe; CaTe; ScN, ScAs, ScSb; YAs; LaAs, and LaSb.

(A) The βR values for the solids of this category lie between 1.18 and 1.65; their γ values range from 1.18 to 5.3 (cf. Table II). They may be considered as typically of the type of alkali halides under higher electrostatic compression. All these are observed to crystallize in the $B1$ structure.

We see from Tables XII and XIII that for these salts only the anion shells with $n = 1$, 2, and 3 contribute to ΔE_1 in the $B1$, $B3$, and $B4$ structures, whereas in the $B2$ configuration anion shells with $n = 1$, 2, 3, 4, and 5 must be taken into account.

Regarding the factors $(1 + E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)})$ for these shells, we have assumed in II for alkali-halide crystals the value $+0.5$ for the nearest neighbors in the $B1$ and $B2$ structures, and a value -1 for the first shell of anions. One possibility is to extend this scheme and to weigh also further shells of anions by a factor -1. We have also varied the weighting factor of the first anion shell by placing it progressively more in the repulsive field of the central anion, with values for $(1 + E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)})$ of -0.5; 0 and $+0.5$. In the $B3$ and $B4$ structures, the first anion shell is farther away from the central anion, namely at a distance $(8/3)^{1/2}R$, compared with $2^{1/2}R$ and $(4/3)^{1/2}R$ in the $B1$ and $B2$ structures, respectively. Consequently, we have associated with the first anion shell in $B3$ and $B4$ the factor -1, i.e., we assume $E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)} = -2$ for that shell. The four

TABLE XII. Madelung energy in kcal/mole; pair energy in units of nearest-neighbor repulsion α_1, and first-order three-ion energy per shell of ions, in units of α_1, for solids of II-VI compounds. The columns labeled 1–9 refer to triplets $A_0A_nA_n$ plus $C_0C_nC_n$, with $n=1, 2, \cdots 9$.

	Madelung energy kcal/mole	Pair energy	$A_0C_1C_1+C_0A_1A_1$	Three-ion energy per shell 1	2	3	4	5	6	7	8	9
BeO; $\beta R=0.99$, $\gamma=30.07$												
*B*1	−1406	93.631	−8.882	−47.601	−3.581	−48.311	−0.717	−4.937	···	···	···	···
*B*2	−1418	132.683	−17.337	−49.717	−24.570	−11.517	−1.033	−35.749	−13.761	···	···	···
*B*3	−1318	51.431	−3.179	−24.570	−1.033	−13.761	···	···	···	···	···	···
*B*4	−1321	51.466	−3.179	−24.558	−1.397	+0.016	−9.331	−2.039	···	···	···	···
MgO; $\beta R=1.26$, $\gamma=5.328$												
*B*1	−1105	15.566	−4.976	−4.989	−0.114	−1.425	···	···	···	···	···	···
*B*2	−1115	22.681	−12.148	−6.852	−2.532	−0.544	−0.016	···	···	···	···	···
*B*3	−1036	8.311	−1.205	−2.532	−0.016	···	···	···	···	···	···	···
*B*4	−1038	8.331	−1.205	−2.544	−0.030	···	···	···	···	···	···	···
CaO; $\beta R=1.44$, $\gamma=1.932$												
*B*1	−966.9	8.670	−3.777	−1.556	−0.010	···	···	···	···	···	···	···
*B*2	−975.3	12.799	−9.861	−2.102	−0.595	−0.058	···	···	···	···	···	···
*B*3	−906.3	4.920	−0.131	−0.595	···	···	···	···	···	···	···	···
*B*4	−907.9	4.937	−0.131	−0.597	···	···	···	···	···	···	···	···
SrO; $\beta R=1.524$, $\gamma=1.225$												
*B*1	−913.6	8.177	−3.867	−1.320	−0.003	···	···	···	···	···	···	···
*B*2	−921.5	12.008	−9.480	−1.702	−0.442	−0.018	···	···	···	···	···	···
*B*3	−856.4	4.652	−0.200	−0.442	···	···	···	···	···	···	···	···
*B*4	−857.9	4.671	−0.200	−0.443	···	···	···	···	···	···	···	···
BaO; $\beta R=1.65$, $\gamma=1.177$												
*B*1	−843.8	7.591	−3.477	−1.069	···	···	···	···	···	···	···	···
*B*2	−851.1	11.383	−9.171	−1.366	−0.284	···	···	···	···	···	···	···
*B*3	−791.0	4.364	+0.033	−0.284	···	···	···	···	···	···	···	···
*B*4	−792.4	4.380	+0.033	−0.284	···	···	···	···	···	···	···	···
BeS; $\beta R=0.9345$, $\gamma=54.66$												
*B*1	−1105	183.005	−9.555	−101.386	−8.894	−117.184	−2.166	−15.833	···	···	···	···
*B*2	−1115	257.253	−18.462	−93.269	−52.387	−26.042	−2.844	−91.551	−38.763	−0.372	···	···
*B*3	−1036	102.216	−3.509	−52.387	−2.844	−38.763	−0.372	···	···	···	···	···
*B*4	−1038	102.263	−3.509	−52.301	−3.557	+0.068	−25.998	−6.475	−0.082	···	···	···
MgS; $\beta R=1.155$, $\gamma=9.69$												
*B*1	−894.2	27.090	−6.659	−10.847	−0.429	−5.753	···	···	···	···	···	···
*B*2	−902.0	39.237	−14.122	−14.100	−5.664	−1.779	−0.083	−3.480	···	···	···	···
*B*3	−838.2	14.361	−2.124	−5.664	−0.083	···	···	···	···	···	···	···
*B*4	−839.7	14.384	−2.124	−5.686	−0.138	···	···	···	···	···	···	···
CaS; $\beta R=1.259$, $\gamma=3.51$												
*B*1	−820.0	12.121	−4.355	−3.144	−0.071	−0.895	···	···	···	···	···	···
*B*2	−827.1	17.512	−11.256	−4.325	−1.581	−0.341	−0.010	···	···	···	···	···
*B*3	−768.6	6.752	−0.606	−1.581	−0.010	···	···	···	···	···	···	··
*B*4	−770.0	6.772	−0.606	−1.588	−0.019	···	···	···	···	···	···	···
SrS; $\beta R=1.335$, $\gamma=2.23$												
*B*1	−773.5	9.609	−4.187	−1.932	−0.025	···	···	···	···	···	···	···
*B*2	−780.2	13.994	−10.449	−2.650	−0.850	−0.134	−0.002	···	···	···	···	···
*B*3	−725.1	5.444	−0.329	−0.850	−0.002	···	···	···	···	···	···	···
*B*4	−726.3	5.464	−0.329	−0.855	−0.005	···	···	···	···	···	···	···
BaS; $\beta R=1.415$, $\gamma=1.54$												
*B*1	−729.7	8.683	−4.092	−1.513	−0.009	···	···	···	···	···	···	···
*B*2	−736.0	12.660	−9.861	−2.013	−0.589	−0.054	···	···	··	···	···	···
*B*3	−684.0	4.934	−0.304	−0.589	···	···	···	···	···	···	···	···
*B*4	−685.2	4.954	−0.304	−0.592	···	···	···	···	···	···	···	···
BeSe; $\beta R=0.8932$, $\gamma=65.67$												
*B*1	−1055	239.708	−9.700	−137.071	−13.189	−172.020	−3.651	−27.783	−0.190	···	···	···
*B*2	−1064	334.764	−18.671	−115.141	−71.705	−36.458	−4.684	−141.407	−63.239	−0.799	−14.442	···
*B*3	−988.7	135.960	−3.597	−71.705	−4.684	−63.239	−0.799	···	···	···	···	···
*B*4	−990.4	135.984	−3.597	−71.585	−5.501	+0.137	−42.026	−11.149	−0.167	···	···	···
MgSe; $\beta R=1.104$, $\gamma=11.64$												
*B*1	−853.1	33.676	−7.075	−14.317	−0.698	−9.647	−0.078	···	···	···	···	···
*B*2	−860.5	48.389	−14.632	−17.687	−7.388	−2.709	−0.154	−6.236	−1.918	···	···	···
*B*3	−799.7	18.078	−2.341	−7.388	−0.154	−1.918	···	···	···	···	···	···
*B*4	−801.1	18.101	−2.341	−7.409	−0.244	0.000	−1.326	···	···	···	···	···
CaSe; $\beta R=1.202$, $\gamma=4.22$												
*B*1	−784.0	14.126	−4.633	−4.106	−0.124	−1.698	···	···	···	···	···	···
*B*2	−790.7	20.260	−11.739	−5.488	−2.110	−0.558	−0.021	−0.926	···	···	···	···
*B*3	−734.9	7.854	−0.829	−2.110	−0.021	···	···	···	···	···	···	···
*B*4	−736.2	7.874	−0.829	−2.119	−0.037	···	···	···	···	···	···	···
SrSe; $\beta R=1.263$, $\gamma=2.67$												
*B*1	−746.2	10.731	−4.470	−2.397	−0.051	−0.642	···	···	···	···	···	···
*B*2	−752.6	15.502	−11.014	−3.310	−1.162	−0.246	−0.007	···	···	···	···	···
*B*3	−699.4	6.077	−0.489	−1.162	−0.007	···	···	···	···	···	···	···
*B*4	−700.7	6.097	−0.489	−1.168	−0.013	···	···	···	···	···	···	···
BaSe; $\beta R=1.344$, $\gamma=1.86$												
*B*1	−701.1	9.253	−4.298	−1.746	−0.020	···	···	···	···	···	···	···
*B*2	−707.1	13.433	−10.295	−2.366	−0.748	−0.105	−0.001	···	···	···	···	···
*B*3	−657.2	5.258	−0.385	−0.748	−0.001	···	···	···	···	···	···	···
*B*4	−658.3	5.278	−0.385	−0.751	−0.004	···	···	···	···	···	···	···
BeTe; $\beta R=0.858$, $\gamma=85.40$												
*B*1	−962.9	336.293	−9.921	−195.845	−20.688	−265.006	−6.171	−49.614	−0.478	···	···	···
*B*2	−971.2	467.522	−19.024	−152.967	−103.594	−54.273	−7.770	−223.430	−104.900	−1.555	−29.472	−10.684
*B*3	−902.6	193.176	−3.715	−103.594	−7.770	−104.900	−1.555	−10.684	···	···	···	···
*B*4	−904.2	193.121	−3.715	−103.330	−8.721	+0.288	−69.156	−19.673	−0.314	−3.012	···	···

TABLE XII (*continued*).

	Madelung energy kcal/mole	Pair energy	$A_0C_1C_1+C_0A_1A_1$	Three-ion energy per shell								
				1	2	3	4	5	6	7	8	9
					MgTe; $\beta R=0.9826$, $\gamma=15.14$							
$B1$	−840.8	51.496	−7.292	−24.441	−1.882	−25.195	−0.388	−2.671	...	...	...	...
$B2$	−848.0	72.432	−14.782	−25.101	−12.533	−5.969	−0.549	−18.879	−7.367	...	...	...
$B3$	−788.1	28.751	−2.525	−12.533	−0.549	−7.367	...	...	...	...	...	...
$B4$	−789.5	28.775	−2.525	−12.525	−0.735	+0.009	−4.987	−1.106	...	...	...	...
					CaTe; $\beta R=1.129$, $\gamma=5.49$							
$B1$	−732.0	18.117	−5.046	−6.015	−0.270	−3.640	−0.027	...	...	...	...	...
$B2$	−738.4	25.753	−12.341	−7.718	−3.159	−1.078	−0.054	−2.302	−0.694	...	...	...
$B3$	−686.2	10.078	−1.166	−3.159	−0.054	−0.694	...	...	...	...	...	...
$B4$	−687.4	10.099	−1.166	−3.169	−0.089	0.000	−0.480	...	...	...	...	...
					SrTe; $\beta R=1.185$, $\gamma=3.48$							
$B1$	−696.9	12.902	−4.758	−3.426	−0.113	−1.538	...	...	...	...	...	...
$B2$	−702.9	18.463	−11.693	−4.549	−1.747	−0.493	−0.020	−0.866	...	...	...	...
$B3$	−653.2	7.297	−0.712	−1.747	−0.020	...	...	...	...	...	...	...
$B4$	−645.4	7.317	−0.712	−1.754	−0.035	...	...	...	...	...	...	...
					BaTe; $\beta R=1.246$, $\gamma=2.41$							
$B1$	−663.0	10.557	−4.703	−2.285	−0.052	−0.658	...	...	...	...	...	...
$B2$	−668.7	15.199	−11.112	−3.144	−1.095	−0.243	−0.007	...	...	...	...	...
$B3$	−621.5	6.006	−0.576	−1.095	−0.007	...	...	...	...	...	...	...
$B4$	−622.6	6.027	−0.576	−1.100	−0.014	...	...	...	...	...	...	...

sets of factors are denoted by $S1$, $S2$, $S3$, and $S4$; in $S1$ the first anion shell of $B1$ and $B2$ has the factor -1; in $S2$, $S3$, and $S4$ these factors are -0.5; 0 and $+0.5$, respectively, both for $B1$ and $B2$. It appears that an increase of these factors for further shells of anions has *very little effect* on stability. To investigate also the sensitivity of the results with respect to the total crystal energy, we have adopted a Born-Mayer model with repulsion exponent p and have taken the values $p=8$ and 9. Different values of p are associated with different values for the nearest-neighbor repulsion α_1, as was explained in a previous section [cf Eq. (13) and the text thereafter].

In the following Table XIV the difference in lattice energy between the structures $B2$ and $B1$, $\delta(B2-B1)$, is given for all salts of category (A), together with the difference $\delta(B4-B1)$ between the $B4$ and $B1$ configurations, in kcal/mole. We can substitute $B3$ for $B4$, since at these large βR values the difference in lattice energy $\delta(B3-B4)$ is vanishingly small. A positive value in the table means that the *second* structure of the difference is the more stable one.

We conclude from Table XIV that the *B1* (*sodium chloride*) *configuration is always the most stable one for II-VI and III-V compounds with relatively large values of βR and relatively small values of γ*. These results are practically independent of the sets of weighting factors ($S1$, $S2$, $S3$, $S4$) for the first shell of anions, i.e., it makes very little difference for stability whether we place the first shell of anions in the attractive or in the repulsive field of the central anion. The results of Table XIV constitute a direct extension of those obtained in II for alkali-halide stability.

(B) The βR values for the solids of this category lie between 0.755 and 0.99; their γ values range from 15 to 177. We remark that for such high γ values, cations play no role at all for the evaluation of the three-ion energy. These solids are typical for $B3$, $B4$ stability.

In view of the very small values of βR, several more shells of anions around a central anion must be considered for the three-ion energy than in (A). It is found that in the $B1$ structure we must generally include six shells of anions, in the $B2$ structure nine, in $B3$ five, and in $B4$ seven shells of anions. Let us first consider the *relative B3, B4 stability*, neglecting for the moment stability of $B1$ and $B2$. As an example we select BN; the peculiarities of three-ion interactions are the same for all salts of this category, as can be verified from Tables XII and XIII. We list, from Table XIII, the three-ion energies ΔE_1 for the different anion shells in units of nearest-neighbor repulsion α_1.

$A_0A_nA_n$	$n=1$	2	3	4	5	6	7
$B3$	−155.320	−14.562	−190.9	−3.915	−29.649	...	...
$B4$	−155.373	−14.913	0.772	−123.111	−39.109	−0.680	−8.236

One sees that the values of ΔE_1 for the first two shells of anions are practically the same. The third shell in $B3$ is at the same distance, $2^{3/2}R$, from the central anion as the fourth shell in $B4$ *and it is in the contributions to* ΔE_1 *from this shell that the first important difference between the B3 and B4 structures arises*. We verify at once that, if $(1+E_{\mathrm{attr}}^{(0)}/E_{\mathrm{rep}}^{(0)})>0$ for this shell, i.e., *if the ions of this shell are in the repulsive field of the central anion, the three-ion attraction in B3 is larger than that in B4, i.e., the B3 structure is more stable*, since all other contributions, including the pair energy and the Madelung energy, are practically identical between $B3$ and $B4$. It is seen that this stabilizing effect of the $B3$ structure is supported to some extent by three-ion

Table XIII. Madelung energy in kcal/mole; pair energy in units of nearest-neighbor repulsion α_1 and first-order three-ion energy per shell of ions, in units of α_1, for solids of III-V compounds. The columns labeled 1–9 refer to triplets $A_0A_nA_n$ plus $C_0C_nC_n$, with $n=1, 2, \cdots, 9$.

	Madelung energy kcal/mole	Pair energy	Three-ion energy per shell									
			$A_0C_1C_1+C_0A_1A_1$	1	2	3	4	5	6	7	8	9
BN; $\beta R=0.7825$, $\gamma=94.65$												
$B1$	−3336	455.859	−9.831	−274.878	−33.060	−413.142	−11.352	−103.891	−1.640	...	...	...
$B2$	−3365	629.239	−18.780	−178.538	−155.320	−79.396	−14.562	−371.067	−190.900	−3.915	−75.847	−29.649
$B3$	−3127	269.709	−3.718	−155.320	−14.562	−190.900	−3.915	−29.649	...	...	...	...
$B4$	−3133	269.067	−3.718	−155.373	−14.913	+0.772	−123.111	−39.109	−0.680	−8.236	...	...
AlN; $\beta R=0.9335$, $\gamma=16.48$												
$B1$	−2797	61.170	−7.206	−30.794	−2.707	−35.669	−0.661	−4.842	...	...	...	...
$B2$	−2821	85.379	−14.574	−28.265	−15.916	−7.916	−0.868	−27.885	−11.824	−0.114	...	...
$B3$	−2621	34.695	−2.525	−15.916	−0.868	−11.824	−0.114	...	...	...	...	...
$B4$	−2626	34.715	−2.525	−15.889	−1.084	+0.020	−7.929	−1.979	−0.025	...	...	...
ScN; $\beta R=1.11$, $\gamma=5.02$												
$B1$	−2352	17.411	−5.024	−5.660	−0.271	−3.721	−0.029	...	...	...	...	...
$B2$	−2372	24.668	−12.302	−7.084	−2.934	−1.058	−0.058	−2.394	−0.727	...	...	...
$B3$	−2204	9.798	−1.057	−2.934	−0.058	−0.727	...	...	...	...	...	...
$B4$	−2208	9.818	−1.057	−2.942	−0.093	0.000	−0.503	...	...	...	...	...
YN; $\beta R=1.219$, $\gamma=2.64$												
$B1$	−2141	11.121	−4.809	−2.546	−0.067	−0.892	...	...	...	...	...	...
$B2$	−2160	15.974	−11.368	−3.430	−1.223	−0.307	−0.010	−0.479	...	...	...	...
$B3$	−2007	6.329	−0.634	−1.223	−0.010	...	...	...	...	...	...	...
$B4$	−2010	6.350	−0.634	−1.229	−0.019	...	...	...	...	...	...	...
LaN; $\beta R=1.325$, $\gamma=1.777$												
$B1$	−1969	9.359	−4.438	−1.772	−0.022	...	...	...	...	...	...	...
$B2$	−1986	13.523	−10.377	−2.392	−0.767	−0.112	−0.002	...	...	...	...	...
$B3$	−1846	5.323	−0.481	−0.767	−0.002	...	...	...	...	...	...	...
$B4$	−1849	5.343	−0.481	−0.770	−0.004	...	...	...	...	...	...	...
BP; $\beta R=0.786$, $\gamma=147.90$												
$B1$	−2657	695.804	−10.359	−422.734	−50.525	−632.396	−17.281	−157.033	−2.426	...	...	...
$B2$	−2680	961.118	−19.735	−276.896	−238.217	−121.784	−22.156	−566.978	−290.607	−5.871	−113.555	−44.378
$B3$	−2490	410.743	−3.943	−238.217	−22.156	−290.607	−5.871	−44.378	...	...	...	...
$B4$	−2495	409.827	−3.943	−238.264	−22.764	+1.156	−187.588	−59.299	−1.032	−12.337	...	...
AlP; $\beta R=0.944$, $\gamma=25.75$												
$B1$	−2212	89.448	−8.451	−46.883	−4.019	−53.066	−0.951	−6.841	...	...	...	...
$B2$	−2231	125.508	−16.512	−44.069	−24.163	−11.939	−1.249	−41.191	−17.186	−0.153	...	...
$B3$	−2074	50.160	−3.032	−24.163	−1.249	−17.186	−0.153	...	...	...	...	...
$B4$	−2077	50.188	−3.032	−24.127	−1.589	+0.028	−11.545	−2.811	−0.034	...	...	...
LaP; $\beta R=1.2026$, $\gamma=2.78$												
$B1$	−1736	11.505	−4.881	−2.724	−0.078	−1.066	...	...	...	...	...	...
$B2$	−1751	16.497	−11.527	−3.639	−1.329	−0.351	−0.013	−0.581	...	...	...	...
$B3$	−1628	6.550	−0.675	−1.329	−0.013	...	...	...	...	...	...	...
$B4$	−1631	6.570	−0.675	−1.335	−0.023	...	...	...	...	...	...	...
BAs; $\beta R=0.755$, $\gamma=177.6$												
$B1$	−2524	911.078	−10.475	−557.090	−70.234	−867.209	−25.049	−239.710	−4.373	...	...	...
$B2$	−2546	1256.838	−19.917	−339.252	−321.353	−164.229	−32.767	−795.363	−422.549	−9.516	−186.566	−74.514
$B3$	−2366	544.633	−4.008	−321.353	−32.767	−422.549	−9.516	−74.514	...	...	...	...
$B4$	−2370	542.637	−4.008	−321.801	−32.759	+1.905	−269.654	−88.327	−1.516	−20.498	...	...
AlAs; $\beta R=0.8906$, $\gamma=30.93$												
$B1$	−2140	119.261	−8.549	−65.674	−6.365	−82.999	−1.773	−13.506	−0.095	...	...	...
$B2$	−2158	166.052	−16.602	−54.863	−34.384	−17.522	−2.269	−68.293	−30.660	−0.393	−7.104	...
$B3$	−2006	68.086	−3.110	−34.384	−2.269	−30.660	−0.393	...	...	...	...	...
$B4$	−2009	68.098	−3.110	−34.307	−2.655	+0.068	−20.362	−5.431	−0.081	...	...	...
ScAs; βR; 1.0014, $\gamma=9.42$												
$B1$	−1903	33.053	−5.939	−14.175	−1.018	−13.874	−0.198	−1.352	...	...	...	...
$B2$	−1919	46.344	−13.256	−15.036	−7.312	−3.345	−0.287	−10.069	−3.854	...	...	...
$B3$	−1784	18.608	−1.843	−7.312	−0.287	−3.854	...	...	...	...	...	...
$B4$	−1787	18.628	−1.843	−7.310	−0.395	+0.004	−2.617	−0.553	...	...	...	...
YAs; $\beta R=1.056$, $\gamma=4.95$												
$B1$	−1805	18.488	−5.301	−6.247	−0.373	−5.012	−0.055	...	...	...	...	...
$B2$	−1820	26.026	−12.614	−7.226	−3.216	−1.326	−0.090	−3.462	−1.198	...	...	...
$B3$	−1692	10.555	−1.107	−3.216	−0.090	−1.198	...	...	...	...	...	...
$B4$	−1695	10.574	−1.107	−3.221	−0.135	0.000	−0.820	...	...	...	...	...
LaAs; $\beta R=1.118$, $\gamma=3.33$												
$B1$	−1705	13.588	−5.394	−3.656	−0.165	−2.248	−0.017	...	...	...	...	...
$B2$	−1720	19.301	−12.372	−4.635	−1.842	−0.650	−0.034	−1.437	−0.432	...	...	...
$B3$	−1598	7.781	−0.949	−1.842	−0.034	−0.432	...	...	...	...	...	...
$B4$	−1601	7.801	−0.949	−1.848	−0.055	0.000	−0.299	...	...	...	...	...
AlSb; $\beta R=0.832$, $\gamma=40.24$												
$B1$	−1963	176.272	−8.708	−100.891	−11.220	−142.084	−3.532	−29.547	−0.345	...	...	...
$B2$	−1980	243.863	−16.799	−74.117	−54.780	−28.462	−4.496	−122.943	−59.619	−1.007	−19.036	−7.059
$B3$	−1840	102.641	−3.216	−54.780	−4.496	−59.619	−1.007	−7.059	...	...	...	...
$B4$	−1843	102.558	−3.216	−54.691	−4.863	+0.183	−39.018	−11.480	−0.194	−1.984	...	...
ScSb; $\beta R=0.9374$, $\gamma=12.25$												
$B1$	−1782	46.615	−6.303	−22.338	−1.946	−25.657	−0.470	−3.418	...	...	...	...
$B2$	−1798	64.898	−13.509	−20.685	−11.533	−5.723	−0.617	−20.007	−8.434	−0.079	...	...
$B3$	−1670	26.582	−2.097	−11.533	−0.617	−8.434	−0.079	...	...	...	...	...
$B4$	−1673	26.599	−2.097	−11.515	−0.775	+0.014	−5.659	−1.400	−0.017	...	...	...
LaSb; $\beta R=1.036$, $\gamma=4.34$												
$B1$	−1613	17.470	−5.695	−5.699	−0.362	−4.881	−0.060	...	...	...	...	...
$B2$	−1627	24.572	−12.985	−6.394	−2.900	−1.246	−0.090	−3.435	−1.239	...	...	...
$B3$	−1512	10.063	−1.176	−2.900	−0.090	−1.239	...	...	...	...	...	...
$B4$	−1514	10.082	−1.176	−2.902	−0.132	+0.001	−0.846	...	...	...	...	...

TABLE XIV. Difference $\delta(B2-B1)$ in static lattice energy between the $B1$ and $B2$ structures, and difference $\delta(B4-B1)$ between the $B1$ and the $B4$ configurations, in kcal/mole, for solids of II-VI and III-V compounds with large values of βR, as a function of the repulsion parameter p. The different sets $S1$, $S2$, $S3$, $S4$ of values for the weighting factors are given in the text For each salt the first line refers to $p=8$ and the second line to $p=9$.

	$\delta(B2-B1)$ in kcal/mole				$\delta(B4-B1)$ in kcal/mole			
	$S1$	$S2$	$S3$	$S4$	$S1$	$S2$	$S3$	$S4$
MgO	39.4	39.0	38.5	37.7	1.9	12.4	26.6	46.7
	33.9	33.6	33.1	32.5	9.1	18.5	31.1	49.0
CaO	24.6	23.6	22.4	20.9	17.3	25.4	35.4	48.0
	20.9	20.0	19.0	17.7	21.9	29.1	38.0	49.2
SrO	20.2	19.8	19.2	18.5	17.2	24.4	33.2	44.0
	17.1	16.7	16.2	15.6	21.5	27.9	35.7	45.3
BaO	16.0	15.5	14.9	14.1	17.3	23.3	30.3	38.8
	13.4	12.9	12.4	11.8	21.1	26.4	32.7	40.2
CaS	23.0	21.8	20.2	18.1	6.5	13.9	23.4	36.0
	19.7	18.6	17.2	15.3	11.4	17.9	26.3	37.6
SrS	23.3	22.6	21.7	20.6	13.3	20.5	29.5	41.1
	19.9	19.4	18.6	17.6	17.1	23.4	31.4	41.7
BaS	18.6	18.0	17.4	16.6	13.6	19.7	27.3	36.8
	15.8	15.3	14.8	14.0	17.0	22.5	29.2	37.7
CaSe	25.0	24.9	24.7	24.4	2.9	9.9	18.9	31.2
	21.5	21.3	21.1	20.9	7.9	14.1	22.1	33.0
SrSe	18.8	17.6	16.1	14.2	8.8	15.4	23.6	34.3
	16.0	14.9	13.6	11.9	12.9	18.7	26.1	35.6
BaSe	20.0	19.4	18.7	17.9	12.8	19.1	27.0	37.0
	17.1	16.6	16.0	15.2	16.1	21.7	28.7	37.6
SrTe	20.2	19.9	19.5	19.0	4.2	10.3	18.0	28.3
	17.2	17.0	16.7	16.2	8.5	13.9	20.7	29.8
BaTe	15.8	14.8	13.6	12.0	8.2	14.0	21.2	30.6
	13.4	12.5	11.4	10.0	11.8	16.9	23.4	31.7
YN	58.3	56.5	54.2	51.1	22.6	41.1	64.4	94.9
	50.0	48.4	46.3	43.6	34.3	50.8	71.6	98.8
LaN	56.9	55.5	53.8	51.6	35.6	53.5	75.8	104.4
	49.7	48.5	46.9	45.0	43.8	60.0	80.1	106.0
LaP	47.3	46.1	44.5	42.4	16.2	31.3	50.3	75.1
	40.4	39.3	37.9	36.1	26.2	39.5	56.4	78.5

contributions from more distant shells of ions. On the other hand, if $(1+E_{\mathrm{attr}}{}^{(0)}/E_{\mathrm{rep}}{}^{(0)})<0$ for the third, respectively fourth, shell of the $B3$ and $B4$ structures, i.e., *if the ions of this shell are in the attractive field of the central anion, the three-ion repulsion in B3 is larger than that in B4, i.e., the B4 structure is more stable.* The first case ($B3$ stability) will occur for the *smallest* values of βR, the latter ($B4$ stability) if βR is larger than a critical value, in striking agreement with experimental observation. It has been verified that the contributions to ΔE_1 from shells at still larger distances may be neglected.

The relative stability of the $B3$, $B4$ configurations is determined completely by the contributions to the three-ion energy $E\{3\}$ from triplets formed by a central anion and two anions from a specific shell around it (the third anion shell in $B3$ and the fourth anion shell in $B4$). To assess the stability of $B3$ and $B4$ with respect to $B1$ and $B2$, on the other hand, closer attention must be paid to the weighting factors $(1+E_{\mathrm{attr}}{}^{(0)}/E_{\mathrm{rep}}{}^{(0)})$ for each shell of anions, since the details of the stability *sequence* for the four structures appear to be a rather sensitive function of these weighting factors.

To illustrate this, we consider the following sets of weighting factors. In the case of $B3$ stability (smallest values of βR) all anion shells in the repulsive field of the central anion are weighted by a factor 0.5; all those in the attractive field by -1, as the simplest extension of the procedure followed for alkali-halide crystals. In the $B1$ configuration there are four anion shells in the repulsive field and two in the attractive field of the central ion. For the remaining structures this subdivision is six and three for $B2$, three and two for $B3$, four and three for $B4$, respectively. We find that for this set of weighting factors the sequence, in order of decreasing stability, is

$$B3>B1>B2>B4,$$

for values $p=7$, 8, and 9 of the Born-Mayer repulsion exponent. It is seen that, although $B3$ is indeed the most stable structure, the $B1$ and $B2$ configurations have higher stability than $B4$.

On the other hand, if we weigh all shells in the repulsive field of the central anion by a factor 0.4 instead of 0.5, then the stability sequence reads

$$B3>B1>B4>B2,$$

again for $p=7$, 8, or 9. Here, although $B3$ is again the most stable structure, the relative stability of $B2$ and $B4$ is reversed.

Certainly, the above *one-step* functions for

$$(1+E_{\mathrm{attr}}{}^{(0)}/E_{\mathrm{rep}}{}^{(0)})$$

are only crude approximations, and it must be expected that more accurate results are obtained by a more gradual dependence of the weighting factors on the distance between shells and central anion. We have for this reason also used a *two-step* function for

$$(1+E_{\mathrm{attr}}{}^{(0)}/E_{\mathrm{rep}}{}^{(0)}),$$

namely a factor 0.5 for the first few anion shells, and 0.25 for the remaining shells in the repulsive field of the central anion; those in the attractive field are weighted by a factor -1.0. In this case the following stability sequence is obtained

$$B3>B4>B1>B2,$$

again for values $p=7$, 8, and 9 of the repulsion exponent. The factor 0.5 is associated with the first two shells in $B1$ and with the first three shells in $B2$, whereas in $B3$ and $B4$ only the first shell of anions falls in this category. With the next shells which are in the repulsive field of the central anion, i.e., shell three and four in $B1$, shell four, five, and six in $B2$, shell two and three in $B3$, and shell two, three, and four in $B4$, we associate the weighting factor 0.25. An increase of weighting factors for shells in the attractive field of the central anion to -1.5 and -2.0 produces the same stability sequence. Consequently, *the theory predicts B3 as the most stable structure for the smallest occurring values of βR, followed by B4, B1, and B2, in this order.* The detailed results for all II-VI and III-V compounds with $B3$ stability are given in the following Table XV.

Finally, in passing to larger βR values, i.e., in going towards $B4$ stability, we must remove certain anion shells from the repulsive field of the central anion and place them, according to the discussion given earlier, in the attractive field. A detailed analysis was undertaken for the subdivision (2.4) for $B1$, (4.5) for $B2$, (2.3) for $B3$, and (2.5) for $B4$. The first number in the parentheses denotes the number of anion shells in the repulsive field, the second number that of anion shells in the attractive field of the central anion. Weighting factors for shells in the repulsive field were taken as 0.5 and 0.4; shells in the attractive field were weighted by a factor -1.0. The order of stability is found to be

$$B4>B3>B1>B2,$$

for values $p=7$, 8, and 9 of the repulsion exponent. Changes in the weighting factors for shells in the attractive field of the central anion do not affect this sequence. Explicit results for crystals of the corresponding compounds with $B4$ stability are given in Table XVI. As in the case of the compounds with $B3$ stability we use a *two-step* function for $(1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)})$; namely, a factor 0.5 is associated with shell one in the $B1$, $B3$, $B4$ and with shell one and two in the $B2$ configurations; with the next shells which are in the repuslive field of the central anion we associate the factor 0.25. The anion shells in the attractive field are all weighted by a factor -1.0.

TABLE XV. Static lattice energy (absolute values in kcal/mole) for II-VI and III-V compounds with the smallest values of βR, in the $B1$ and $B2$, $B3$ and $B4$ structures, for values $p=7$, 8, and 9 of the Born-Mayer repulsion exponent. A *two-step* function (0.5; 0.25), as given in the text, is used for the weighting factors of anion shells in the repulsive field of the central anion. For the anion shells in the attractive field the weighting factors are, respectively: (-1.5; -2.0) for the $B1$; (-1.5; -2.0; -2.0) for the $B2$; (-1.5; -2.0) for the $B3$ and (-1.5;-1.5;-2.0) for the $B4$ configuration. For each salt the first line refers to $p=7$, the second line to $p=8$, the third line to $p=9$.

	$B3$	$B4$	$B1$	$B2$
BeS	888	861	836	817
	906	883	869	853
	921	901	896	884
BeSe	848	814	785	737
	865	835	818	776
	879	853	844	809
BeTe	774	755	743	684
	790	774	770	719
	803	789	792	748
BN	2680	2626	2569	2300
	2736	2689	2665	2434
	2780	2739	2741	2538
BP	2135	2090	2044	1830
	2179	2140	2120	1935
	2214	2180	2180	2019
BAs	2028	1994	1946	1717
	2070	2041	2018	1820
	2103	2078	2075	1901
AlP	1777	1731	1691	1655
	1815	1775	1757	1728
	1843	1808	1807	1783
AlAs	1719	1652	1601	1512
	1755	1697	1669	1593
	1783	1738	1721	1656
AlSb	1572	1535	1508	1381
	1605	1573	1564	1455
	1631	1603	1608	1513

TABLE XVI. Static lattice energy (absolute values in kcal/mole) for II-VI and III-V compounds with $B4$ stability, in the $B1$, $B2$, $B3$, and $B4$ configurations for values $p=7$, 8, and 9 of the Born-Mayer repulsion. A two-step function 0.5; 0.25 as given in the text is used for the weighting factors of anion shells in the repulsive field of the central anion; the anion shells in the attractive field are weighted by a factor -1.0. For each salt the first line refers to $p=7$, the second line to $p=8$, and the third line to $p=9$.

	$B4$	$B3$	$B1$	$B2$
BeO	1130	1118	941	895
	1153	1142	997	958
	1172	1162	1043	1010
MgTe	676	669	575	551
	690	683	607	587
	702	696	635	618
AlN	2251	2225	1914	1822
	2298	2274	2025	1947
	2334	2312	2110	2043

(C) The βR values for the solids of this third category lie between 0.94 and 1.15; their γ values range from 3.3 to 12.2 (cf. Table II). Although these compounds are all observed to be stable in the $B1$ configuration, their $(\beta R,\gamma)$ values are in a range intermediate between those typical for $B1$ and those for $B3$, $B4$ stability.

Correspondingly, the weighting factors for anion shells are chosen in between those for categories (A) and (B). Compared with the case of $B4$ stability we remove *one more shell* of anions from the repulsive field of the central anion, so that the subdivision of shells becomes (1.5) for $B1$, (2.7) for $B2$, (1.4) for $B3$, and (1.6) for $B4$. The shells in the repulsive field are weighted by factors 0.5 for $n=1$ in the $B1$ and $B2$ configurations; for $n=1$ in the $B3$ and $B4$, and also for $n=2$ in the $B2$ configurations we use different values of the weighting factor, namely, 0.25 (set $S5$), 0.20 (set $S6$), and 0.1 (set $S7$). Since the further shells are now relatively far in the attractive field, we use for all sets 5–7, a gradually varying function for the quantity $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$; denoting by d the distance of a shell from the central anion, the weighting factors are chosen as follows: -1.0 for $2R\leqslant d\leqslant 6^{1/2}R$, -1.5 for $(20/3)^{1/2}R\leqslant d\leqslant (8/3)R$, and -2.0 for $d\geqslant 8^{1/2}R$, where R denotes the nearest-neighbor distance. For these sets of weighting factors the stability sequence is found to be

$$B1>B4>B3>B2,$$

for $p=8$ and 9 of the Born-Mayer repulsion. The $B2$, $B3$ order can be reversed by minor changes in the weighting factors, but it is not essential to consider such changes. In Table XVII detailed results are given for all II-VI and III-V compounds of this category. It is of interest to note the decrease in stability of the $B2$ configuration for the intermediate values of βR compared to its stability at larger βR values (Table XIV).

TABLE XVII. Static lattice energy in kcal/mole, for II-VI and III-V compounds with intermediate values of βR and γ, in the $B1$, $B2$, $B3$, and $B4$ configurations, for values $p=8$ and 9 of the Born-Mayer repulsion exponent. The weighting factors for anion shells in the repulsive or attractive fields of the central anion are described in the text. For each salt the first line refers to $p=8$ and the second line to $p=9$.

	Set $S5$				Set $S6$				Set $S7$			
	$B1$	$B4$	$B3$	$B2$	$B1$	$B4$	$B3$	$B2$	$B1$	$B4$	$B3$	$B2$
MgS	783	780	775	748	783	778	773	747	783	775	770	744
	795	787	782	765	795	785	780	764	795	783	778	761
MgSe	747	746	740	707	747	744	738	706	747	733	727	681
	758	752	746	724	758	751	745	723	758	741	736	703
CaTe	641	635	629	613	641	634	628	612	641	632	626	610
	651	641	635	627	651	640	634	626	651	638	633	624
ScN	2058	2031	2020	2002	2058	2028	2018	2000	2058	2023	2012	1994
	2091	2051	2041	2044	2091	2048	2039	2042	2091	2044	2034	2037
ScAs	1655	1650	1636	1522	1655	1635	1619	1520	1655	1629	1614	1515
	1692	1671	1658	1558	1692	1648	1633	1555	1692	1643	1629	1550
YAs	1579	1559	1545	1511	1579	1557	1543	1509	1579	1552	1539	1505
	1604	1574	1561	1545	1604	1552	1560	1544	1604	1568	1556	1540
LaAs	1492	1467	1465	1476	1492	1466	1463	1474	1492	1463	1461	1470
	1516	1482	1480	1503	1516	1481	1478	1501	1516	1478	1476	1499
ScSb	1560	1546	1540	1498	1560	1545	1538	1496	1560	1542	1536	1494
	1584	1560	1554	1530	1582	1559	1553	1529	1582	1546	1550	1526
LaSb	1411	1386	1381	1376	1411	1385	1379	1374	1411	1382	1377	1372
	1434	1401	1395	1404	1434	1400	1394	1403	1433	1397	1392	1401

DISCUSSION OF RESULTS

The analysis of crystal stability presented in the preceding sections is based on a Born-Mayer model for II-VI and III-V compounds supplemented by three-ion exchange interactions in first and second orders of perturbation theory. As in the case of alkali-halide stability the three-ion interactions are evaluated *relative to* pair potentials between the ions. Such pair interactions are not known with precision for alkali-halide ions; for II-VI and III-V compounds the isolated ions are often not known. However, the only information we need regarding pair potentials are values of the factors $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ for a limited number of shells around a central ion.

In *rare-gas crystals* an atom from the first shell of neighbors and a reference atom attract each other; the factor $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ for this shell is approximately -1 [$-6/(s-6)$ for a Lennard-Jones $(s,6)$ potential]. Contributions from further shells to the three-atom energy can be neglected. In *alkali-halide crystals* an ion from the first shell and a reference ion repel each other; the value of the weighting factor for this shell is now approximately 0.5, which follows from analogy with rare-gas atoms and from a direct evaluation on the basis of the Gaussian approximation (Table XI). For the second shell of ions a factor of -1 is chosen, as for the first shell of rare-gas crystals; further shells can be neglected for stability.

Owing to high electrostatic compression in *solids of II-VI and III-V compounds*, a still larger number of shells of ions must be considered for crystal stability in this case. The interaction between a reference ion and an ion from the first few shells is repulsive, whereas it is attractive for the remaining shells. In this paper we have shown that a consistent explanation of observed crystal stability for II-VI and III-V compounds can be given *on the basis of a gradual variation of the number of ion shells whose interaction with the reference ion is repulsive*, as a function of interionic distances. The value of $1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)}$ is taken as 0.5 for each such shell, and as -1 for the remaining shells. A refinement of this one-step function for the weighting factors sometimes causes a change in the stability sequence for the configurations $B1$, $B2$, $B3$, and $B4$, but the observed structure always remains the most stable one. In varying the weighting factors it was found that the stability margin for the observed structure is relatively large, so that definite conclusions regarding crystal stability can be drawn. Detailed results with different sets of weighting factors are given in Tables XIV and XVII ($B1$ stability), Table XV ($B3$ stability) and Table XVI ($B4$ stability).

Regarding the *relative stability of the B3* (*sphalerite*) *and B4* (*wurtzite*) *configurations* we have found that it is completely determined by the difference in three-anion interactions involving the third shell of anions in $B3$ and the fourth shell in $B4$, which are at the same distance from the reference anion. It is interesting to note that in the case of $B3$ stability (smallest values of βR) this structure is considerably more stable than $B4$, namely, by several percent of the total crystal energy (Table XV). For compounds which are stable in the $B4$ configuration, on the other hand, the difference in lattice energy between $B4$ and $B3$ is always smaller, namely, only 1% (Table XVI).

Next we discuss the *stability of the B2* (*CsCl*) *configuration* as a function of βR. In the case of alkali-halide crystals we found in II that the stability of this structure is associated with *large* values of βR and *small* values of γ. The condition for stability of $B2$ is, specifically, that triplets $A_0C_1C_1$ ($C_0A_1A_1$) provide the predominant contribution to the three-ion energy. This necessitates, on one hand, that anion and cation are of comparable size (small γ values) and, on the other hand, that further shells are at much larger distances, so that these do not develop considerable three-ion repulsion. Because of the second condition (large βR values) the $B2$ configuration *cannot appear* with solids of II-VI and III-V compounds. The results of Tables XII and XIII demonstrate the occurrence of strong and repulsive three-ion contributions from further shells in this structure at relative small values of βR (e.g., for BeTe and MgTe in Table XII; BN, AlN, ScN in Table XIII). We note that, to calculate the total three-ion interactions for such shells, the values of Tables XII and XIII have to be multiplied by the weighting factors of the shells. Since these factors are negative, the three-ion energies for distant shells are repulsive. The decrease in stability of $B2$ with decreasing values of βR is also illustrated by comparing the results of Table XIV and Table XVII.

Finally, regarding the *stability of the B1* (*NaCl*) *configuration*, we find that this structure is the most stable one over a wide range of values for βR and γ, in agreement with the Born-Mayer theory and with the Goldschmidt rules. At relatively large values of βR, the stability of this structure is due to the fact that less three-ion repulsion is developed by further shells compared to $B2$, in addition to the pair repulsion for $B1$ being lower. The development of the $B1$, $B2$ relative stability with decreasing βR values for different sets of weighting factors is illustrated by the results given in Tables XIV and XVII. The set $S1$ of Table XIV is that used for alkali-halide stability; the first shell of ions favors the $B2$ structure, whereas the second shell of ions develops less three-ion repulsion in the $B1$ configuration (see Tables VI and VII of II). In the sequence $S2$, $S3$, $S4$ the weighting factor for the first shell of anions is changed progressively from -0.5 to $+0.5$. Consequently, in the set $S4$ three-ion interactions from the first anion shell around a reference anion *also* favor the $B2$ configuration. Nevertheless the $B2$ stability increases only very little with respect to $B1$, because of larger three-ion repulsion developed by further shells in this configuration. We note that the sequence of anion shells in $B2$ is more dense than in $B1$ (compare Tables VII and VIII).

When the values of βR are further decreased, more distant shells in $B1$ develop three-ion repulsion. At the same time, the interaction between the first shell of anions in the $B3$ and $B4$ configurations and a reference anion become gradually more repulsive, *resulting in attractive three-ion interactions*. As a consequence, crystal stability *shifts towards the B4 structure*; this shift is illustrated by the results of Table XVII (sequence $S7$, $S6$, $S5$).

As in the case of alkali-halide crystals the stability analysis for solids of II-VI and III-V compounds is based on a *single-exchange* approximation (one effective electron per ion). Moreover, we have not considered contributions from *nonisosceles* triangles to the three-ion energy in the four structures. The problem concerning *double-exchange* contributions to the three-ion energy was analyzed in detail in II. It was shown that the symmetry properties of relative three-ion interactions remain the same if double exchange is included, for βR values as low as 1. Such effects can be important only in association with small βR values, i.e., in the region of $B3$ and $B4$ stability. However, we have found that the relative $B3$, $B4$ stability is determined by triplets of anions consisting of a central anion and two anions from the third shell in $B3$ and the fourth shell in $B4$. The distance from these shells to the reference anion is in both cases $8^{1/2}R$, where R is the nearest-neighbor separation. The corresponding βR values for these shells are typical for alkali-halide crystals; consequently, the effect of double exchange on $B3$, $B4$ stability can be neglected. We note also that triplets of anions from the first and second shells in these structures are practically identical, as can be verified from Tables IX and X. The problem concerning *nonisosceles* triangles was also discussed in II; it was found that in the $B1$ and $B2$ configurations contributions from such triangles are small and of the same order of magnitude in either structure. Moreover, they tend to cancel because of symmetry properties of three-ion interactions. The *same* properties are observed to hold for the $B3$ and $B4$ lattices; consequently, we may neglect effects due to nonisosceles triangles in all four structures.

The *relative magnitude* of the total three-ion interactions, with respect to the total pair repulsion in the stable structure, varies between $+26$ and -8% for the compounds of category (A), i.e., for $B1$ stability at large βR values. For compounds of category (C), i.e., for $B1$ stability at smaller βR values, this percentage is generally much lower (between $+3$ and -2%). For solids with $B4$ stability the total three-ion energy varies between $+1.2$ and -5.2% of the pair repulsion. In case of $B3$ stability, however, the three-ion interactions are *large* and *negative* for all compounds; they vary between -25 and -40% of the pair repulsion.

We have thus found that the anomalies of the Born-Mayer theory of ionic solids with respect to the observed stability of the $B2$ configuration on one hand, and of the $B3$, $B4$ structures on the other hand, can be quantitatively explained in terms of three-ion exchange interactions. The extra attractive energy necessary to stabilize the $B2$ structure at large values of βR is provided by three-ion interactions for triplets of the types $A_0C_1C_1$ and $C_0A_1A_1$. The additional attraction in the $B3$ configuration at the smallest values of βR arises from contributions to the three-ion energy from triplets of anions $A_0A_nA_n$ for the first few values of n (numbering shells of anions in this case). The $B4$ structure can be interpreted as a lattice type intermediate between $B1$ and $B3$; its stability is limited to a narrow range of βR values and its total three-ion energy is quenched relative to both $B1$ and $B3$.

So far, we have not considered the effect of d electrons in closed shells on crystal stability of RX compounds; R stands for Cu, Ag; Zn, Cd, Hg; Ga, In. In these cases the structures $B1$, $B2$, $B3$, and $B4$ are also observed, often associated with polymorphic transitions.[19] It may also be expected that the crystal stability for compounds of the type RX_2 (fluorite, rutile, $CdCl_2$, CdI_2, etc.) can be explained in terms of three-ion interactions. Such an analysis is at present under way.

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Temperature Dependence of Dielectric Constants of Crystals with NaCl and CsCl Structure

E. E. Havinga and A. J. Bosman
Philips Research Laboratories, N. V. Philips' Gloeilampenfabrieken, Eindhoven, Netherlands

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The dielectric constant and its temperature and pressure dependence have been measured on RbCl, RbBr and CsCl, CsBr, CsI. The values for ϵ, $10^5(\partial\epsilon/\partial T)_p/(\epsilon-1)(\epsilon+2)$ $(°K)^{-1}$ and $10^7(\partial\epsilon/\partial p)_T/(\epsilon-1)(\epsilon+2)$ $(kg/cm^2)^{-1}$ are 5.0, 5.5, −19.4; 4.9, 5.2, −23.5; 7.2, 2.5, −16.3; 6.5, 2.8, −19.1; and 5.7, 3.2, −23.2, respectively. The temperature dependence for compounds with the CsCl structure thus is smaller than for compounds with the NaCl structure. The existence of a structural effect has been verified by measuring RbBr at 4600 kg/cm² in both structures. The corresponding quantities as given above are in the NaCl structure 4.65, 4.9, −21 and in the CsCl structure 6.5, 2.1, −17. Analysis of the results shows that the difference is due to a difference in the temperature dependence of the infrared polarizability at constant volume. The theory shows that, whereas there is no difference in the negative contribution from fourth-order anharmonic terms in the potential energy to this temperature dependence of the polarizability in both structures, the positive influence of third-order terms increases as the number of nearest neighbors decreases. By using a simple ionic model a semiquantitative agreement between theory and experiment was obtained.

I. INTRODUCTION

In a previous paper[1] it has been shown that three effects contribute to the temperature dependence of the dielectric constant of a cubic material. For such a material the macroscopic Clausius-Mossotti formula holds:

$$(\epsilon-1)/(\epsilon+2)=\tfrac{4}{3}\pi\alpha_m/V\,, \tag{1}$$

where α_m is the polarizability of a macroscopic, small sphere with a volume V in vacuum.

Differentiation of formula (1) with respect to temperature at constant pressure gives

$$\frac{1}{(\epsilon-1)(\epsilon+2)}\left(\frac{\partial\epsilon}{\partial T}\right)_p=-\frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_p+\frac{V}{\alpha_m}\left(\frac{\partial\alpha_m}{\partial V}\right)_T\left(\frac{1}{3V}\right)\left(\frac{\partial V}{\partial T}\right)_p+\frac{1}{3\alpha_m}\left(\frac{\partial\alpha_m}{\partial T}\right)_V=A+B+C. \tag{2}$$

The physical processes described by the terms A, B, and C are

A: the decrease in the number of polarizable particles per unit volume as the temperature rises; the direct effect of the volume expansion;

B: an increase of the polarizability of a constant number of particles with the increase of available volume as the temperature rises;

C: a dependence of polarizability on temperature, the volume remaining constant.

The terms A, B and C can be determined separately by measuring the dielectric constant ϵ, its temperature dependence $(\partial\epsilon/\partial T)_p$ and its pressure dependence $(\partial\epsilon/\partial p)_T$, the thermal expansion coefficient $(1/V)(\partial V/\partial T)_p$ and the compressibility $\kappa=-(1/V)(\partial V/\partial p)_T$. The statement of Fuchs[2] that this separation into three terms involves microscopic theories is incorrect, as was already outlined in a previous paper.[3]

In the case of ionic crystals the polarizability α_m of the macroscopic sphere can be separated into α_m^{op}, the

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