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Crystal Stability of AX_2 Compounds in Terms of Three-Ion Interactions

ERMINIO LOMBARDI* AND LAURENS JANSEN
Battelle Institute, Advanced Studies Center, Geneva, Switzerland
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By taking into account three-ion exchange interactions in solids of AX_2 compounds, it is shown how the observed stability relations can be explained on a quantitative basis. The analysis is an extension of those given earlier for stability of rare-gas crystals, of solids of the alkali halides, and of II-VI and III-V compounds whose ions are isoelectronic with rare-gas atoms. Of the compounds AX_2, A denotes an element of columns II, IV, or VI of the periodic table, X a corresponding element of the columns I, II, VI, or VII. All ions considered are isoelectronic with rare-gas atoms. As before, the stability analysis is based on a first- and second-order perturbation calculation, starting from complete ionicity in zeroth order of approximation, with Gaussian-type effective electron wave functions for the ions. The structures considered are (the ideal lattices of) fluorite, two types of rutile, anatase, cadmium chloride, cadmium iodide, cuprite, quartz, and cristobalite; a comparison is made between the static lattice energies of these structures. The effect of polarization energy on crystal stability is considered in detail in the framework of the Born-Mayer model; Madelung constants for all structures were determined on the basis of the Bertaut method. The theory accounts for all observed stability relations; except that for the compound TiO_2 the fluorite structure is found to be more stable than a rutile lattice on the basis of closed-shell electron configurations of the Ti ion. In particular, a quantitative explanation is given for the difference in lattice energy between the cadmium iodide and cadmium chloride structures (6,3 coordination) and between the β-quartz and β-cristobalite lattices (4,2 coordination).

I. INTRODUCTION

In previous publications we have undertaken a stability analysis for rare-gas crystals,[1] for solids of the alkali halides[2] and for those of II–VI and III–V compounds[3] whose ions are isoelectronic with rare-gas atoms. It was found in all cases that simultaneous exchange interactions between three atoms or three ions constitute the essential short-range, structure-sensitive component of the crystal field. In this paper, a similar analysis is undertaken for crystals of compounds of the type AX_2, whereby we restrict ourselves again to the rare-gas isoelectronic series.

In the analysis we will not consider carbon as one of the constituents (carbides, or molecular compounds such as carbon dioxide). With this limitation, A is an element of columns II, IV, or VI of the periodic table and X is an element of the corresponding columns I, II, VI, or VII. Representatives are OCs_2 (VI-I), CaF_2 (II-VII), SiO_2 (IV-VI), etc. The ideal crystal structures can have 8,4, 6,3, or 4,2 coordination; distorted structures have frequently been found but these will not be considered here. The only lattice type with 8, 4 coordination is *fluorite* ($C1$); to the second category (6,3 coordination) belong the structures known as *rutile* ($C4$), *anatase* ($C5$), *cadmium iodide* ($C6$), and *cadmium chloride* ($C19$). In the category with 4,2 coordination we find the structures *cuprite* ($C3$), *quartz* ($C8$), and *cristobalite* ($C9$). The symbols in parentheses are the Structure Reports notations for the various lattice types.

We note, first, that the stability relations for crystals of AX_2 compounds appear to depend strongly on *whether A or X is the larger ion* of the compound. In the first case (A larger) we always find stability of the fluorite structure; on the other hand, if X is the larger ion, then all possible coordinations are observed. A satisfactory stability theory must reflect this characteristic distinction.

The first stability analysis involving AX_2 compounds was undertaken by Hund.[4] In his model, the ions interact electrostatically as point charges; the non-Coulombic part of the interactions is represented by a short-range repulsion proportional to R^{-p}, where R is the interionic distance. A pair potential of this type, with R^{-p} often replaced by an exponential term and with sometimes an additional van der Waals long-range attraction proportional to R^{-6}, is generally called a Born-Mayer potential. Hund found that no essential structure sensitivity of the potential is lost when the repulsions are restricted to nearest neighbors in the lattice. If we denote the Madelung constant of a given lattice by M, the coordination number of the A ion by Z, then stability is determined uniquely (neglecting thermal effects and zero-point energy) by the value of the parameter $(M^p/Z)^{1/(p-1)}$; the structure with the largest value for this parameter is the most stable one. Hund compared the fluorite, rutile, and cuprite configurations for different values of p and found that, for $p>6$, the fluorite structure is always favored. Since the values of p are expected to lie in the neighborhood of 8 to 10, in analogy with the case of other ionic solids, all AX_2 compounds should crystallize with the *fluorite* structure. This prediction agrees with experiment if A is the larger ion, but with X as the larger ion the agreement is very poor. Therefore,

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

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

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

[3] E. Lombardi and L. Jansen, Phys. Rev. 140, A275 (1965), hereafter referred to as [III].

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

a stability theory for crystals of AX_2 compounds which is based on a Born-Mayer pair potential does not reflect the observed differentiation in crystal structures when X is the larger ion of the compound.

Later analyses[5,6] were based, instead, on a more empirical approach, namely, on the *Goldschmidt rules*. In the model underlying these rules, the ions are represented by rigid spheres; the structure-dependent parameters are then the Madelung constant M, the coordination number Z, and the ratio r_+/r_- between the radii of positive and negative ions. It appears that the predictions from the Goldschmidt rules agree more closely with the observed stability relations; this is not surprising since in these rules the different size of A and X ions enters as an explicit parameter. For a detailed discussion of the Goldschmidt rules we refer to Pauling.[7] Analyses based on these rules were carried out by Goldschmidt[5] and Hund[6] for the three main categories with 8,4,6,3, and 4,2 coordinations.

For our stability analysis it is of interest to pursue the predictions from the Goldschmidt rules a little further. We have therefore extended these considerations by taking into account two different rutile modifications, denoted by rutile I and rutile II, for which the crystallographic parameters are (rutile I) $c/a=(\frac{2}{3})^{1/2}$, $u=\frac{1}{3}$ and (rutile II) $c/a=2^{1/2}/(1+2^{1/2})$, $u=1-2^{-1/2}$. Here, c/a is the axial ratio and u is the z coordinate of the X ion, divided by c. The parameters of all observed rutile structures lie between these two limits. We also included the (ideal) anatase lattice ($c/a=2$, $u=\frac{1}{4}$), as well as the (ideal) cadmium iodide and cadmium chloride modifications; the latter are defined by $\cos\alpha=\frac{5}{6}$, $u=\frac{1}{4}$ for cadmium chloride (α is the rhombohedral angle of the unit cell) and by $c/a=(8/3)^{1/2}$, $u=\frac{1}{4}$ for the cadmium iodide lattice. For the Madelung constants we used values as given in the next section. The results can be described as follows. When A is the larger ion of the AX_2 compounds, the fluorite structure has a broad domain of stability, ranging from $r_+/r_-=1$ (A and X of the same size in the limit) to $r_+/r_-=0.163$. Below the latter value, rutile I becomes first competitive with $C1$, whereas for the smallest values of this parameter (<0.077) the $C8$, $C9$ structures are more stable. Agreement with experiment is very good for this category. The $C6$, $C19$ configurations are always the least stable ones, but their stability is certainly underestimated because polarization energy is not considered. When X is the larger ion, we first find fluorite stability ($r_+/r_->0.636$), but then rutile II takes over, for the whole domain until $r_+/r_-=0.323$ (rutile I behaves abnormally in that it is always the least stable configuration). Finally, if $r_+/r_-<0.323$, we find $C8$ ($C9$) as the most stable structure. Agreement with experiment is very poor for this category, since $C6$ and $C19$ dominate the observed stability relations. Again, it should be remembered that the stability of $C6$ and $C19$ is underestimated in the Goldschmidt rules because polarization energy is not considered, which is particularly important when X is the larger ion of the compound. Except for rutile I, we again find $C6$ and $C19$ at the end of the stability scale. Excluding $C6$ and $C19$, we find very little distinction between structures with the same coordination, since their Madelung constants are practically equal.

Although the differentiation in stability is considerably more pronounced on the basis of the Goldschmidt rules than in the framework of the Born-Mayer model, it is apparent that in both models essential structure-sensitive components of the crystal field are missing. One of these is the polarization energy which increases the stability of the cadmium iodide and cadmium chloride configurations. We will first give the crystal structures for AX_2 compounds and then analyze the first-order (Madelung) and second-order (polarization) components of the electrostatic crystal energy.

II. GAUSSIAN PARAMETERS AND CRYSTAL STRUCTURES FOR AX_2 COMPOUNDS

The analysis of crystal stability for AX_2 compounds presented in this paper is an extension of those given earlier for stability of rare-gas crystals [I], solids of the alklai halides [II], and solids of II-VI and III-V compounds [III]. The three-ion component of the static lattice energy is evaluated, as before, in first and second orders of perturbation theory, using free-ion, effective-electron wave functions of Gaussian type in zeroth order of approximation and taking into account only single-exchange interactions between the ions.

The inverse width β of the Gaussian electron-charge distribution for each ion,

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

where r is the distance from the effective electron to its nucleus, can be determined empirically from values of the diamagnetic susceptibility of the ions,[8] taking the value for the corresponding isoelectronic rare-gas atom as reference (cf. [II]). A compound AX_2 is characterized by two Gaussian parameters β and β', one for the A ion and one for the X ion. We adopt the convention that β denotes the larger, and β' the smaller, ion of the compound, i.e., $\beta'\geqslant\beta$. The three-ion component of the lattice energy, relative to the sum of non-Coulombic pair interactions, is then completely determined by the crystal structure, by the dimensionless parameter βR, where R is the nearest-neighbor distance in the lattice, and by the parameter $\gamma=(\beta'/\beta)^2\geqslant 1$.

In the following Tables I and II we list the values for the parameters βR and γ of AX_2 compounds, as

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[5] V. M. Goldschmidt, Z. Tech. Physik **7**, 251 (1927).

[6] F. Hund, Z. Physik **94**, 11 (1935).

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

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

TABLE I. Values for the Gaussian parameters βR (R is the nearest-neighbor distance in the lattice) and $\gamma=(\beta'/\beta)^2$ for crystals of AX_2 compounds of which A is the larger ion. All these compounds crystallize in the fluorite ($C1$) structure; β represents the larger ion (A) of the compound.

AX_2	βR	γ	AX_2	βR	γ
Li_2O	1.200	18.77	K_2S	1.424	2.60
Li_2S	1.100	34.14	K_2Se	1.350	3.13
Li_2Se	1.056	41.00	K_2Te	1.257	4.07
Li_2Te	1.003	53.34	Rb_2O	1.751	1.00
Na_2O	1.440	3.75	Rb_2S	1.474	1.82
Na_2S	1.258	6.82	CaF_2	1.985	1.24
Na_2Se	1.197	8.19	SrF_2	1.668	1.99
Na_2Te	1.127	10.65	BaF_2	1.482	2.88
K_2O	1.672	1.43	$BaCl_2$	1.754	1.02

well as their crystal structures[9] at normal temperature and pressure. The data of Table I concern AX_2 compounds of which A is the larger ion, whereas the values of Table II refer to those compounds of which X is the larger ion.[10]

III. THE ELECTROSTATIC LATTICE ENERGY

In the Born-Mayer model of ionic solids, the ions interact electrostatically as nonoverlapping charge distributions. The first-order electrostatic energy, per mole of the crystal, is the Madelung energy; the second-order electrostatic contribution is commonly called polarization energy. We assume that the effect of the net ionic charges on *crystal stability* is reflected essentially by the different values of these two components for the different structures. We first analyze the Madelung energy of the lattices and then proceed to the polarization contributions.

A. Madelung Constants for AX_2 Lattices

Several methods are available in the literature for calculating the Madelung energy of a given type of structure and ions which interact electrostatically as point charges (nonoverlapping charge distributions). Extensive reviews of these methods and of the results obtained by different authors for solids of composition AX, AX_2, and for more complicated structures are given by Waddington[11] and Tosi[12]; we refer to these reviews for a general discussion. Among the structures occurring for AX_2 compounds which we have specified earlier, the only missing Madelung constant is that of the (ideal) cadmium chloride lattice. For cadmium iodide, Waddington reports values determined by Hund[4] for different parameters of the axial ratio c/a and of u, the z coordinate of the position of the iodide ion, divided by c. For the structure closest to the ideal one, the Madelung constant reported is 4.71, differing only slightly from the value of 4.72 for rutile types. The values for cadmium iodide are surprisingly high, considering the layer type of structure for this compound, which is expected to result in a lowering of the Madelung constant as compared with more symmetric arrangements of ions with the same coordination, as in rutile. Indeed, a more recent calculation by Johnson and Templeton[13] for two common forms of cadmium iodide yields an average value of 4.38, corresponding accurately to a value for these two types determined earlier by Hartmann.[14] Johnson and Templeton obtained a value of 4.489 for the mineral cadmium chloride, about 2% higher than the Madelung constants for the cadmium iodide structures. The lattice of the mineral cadmium chloride deviates considerably from the ideal configuration, for which the Madelung constant is not available in the literature.

TABLE II. Values for the Gaussian parameters βR (R is the nearest-neighbor distance in the lattice) and $\gamma=(\beta'/\beta)^2$ for crystals of AX_2 compounds of which X is the larger ion, and their crystal structure observed at normal temperature and pressure. The parameter β represents the larger ion (X) of the compound.

AX_2	βR	γ	Structure[a]	AX_2	βR	γ	Structure[a]
Cs_2O	1.470	1.42	$C19$	TiS_2	1.072	7.60	$C6$
BeF_2	1.468	12.28	$C8$-$C9$	$TiSe_2$	1.016	9.13	$C6$
MgF_2	1.860	2.17	$C4$	$TiTe_2$	0.945	11.90	$C6$
$MgCl_2$	1.417	6.12	$C19$	ZrO_2	1.317	2.20	$C1$
$MgBr_2$	1.290	8.30	$C6$	ZrS_2	1.152	4.00	$C6$
MgI_2	1.227	10.85	$C6$	$ZrSe_2$	1.082	4.81	$C6$
CaI_2	1.327	4.00	$C6$	$ZrTe_2$	0.994	6.26	$C6$
$SrCl_2$	1.686	1.42	$C1$	HfO_2	1.329	1.54	$C1$
SiO_2	0.912	15.42	$C8$-$C9$	HfS_2	1.143	2.80	$C6$
$SiTe_2$	1.077	43.34	$C6$	$HfSe_2$	1.076	3.37	$C6$
TiO_2	1.146	4.18	$C4$-$C5$				

[a] $C1$ =fluorite, $C4$ =rutile, $C5$ =anatase, $C6$ =cadmium iodide, $C8$ =β-quartz, $C9$ =β-cristobalite, $C19$ =cadmium chloride.

We have calculated the Madelung constants following the Bertaut method,[15] which method was also used by Johnson and Templeton. Bertaut showed that, in replacing the ions by spherically symmetric, nonoverlapping charge distributions, the Madelung constant of a lattice is obtained as a single, infinite, series which is absolutely convergent and whose terms are functions of the reciprocal lattice vectors. The convergence properties of the Bertaut series for different forms of the charge distributions, and cutoff errors, were investigated by Jones and Templeton.[16] Details of the Bertaut method will be given below in connection with the calculation of the polarization energy.

The determination of Madelung constants was carried out for the ideal lattices (in all cases), using a charge distribution for the ion at position $\mathbf{r}_j$, of the form $\sigma_j(|\mathbf{r}-\mathbf{r}_j|)=a(|\mathbf{r}-\mathbf{r}_j|)^p$ with $p=0$, 1, 2, and 3, re-

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[9] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1963), 2nd ed., Vol. 1.

[10] Although Hf^{4+} is not isoelectronic with a rare-gas atom we have included Hf compounds in Table II, since the Hf^{4+} ion also has a closed 8 electron (s,p) shell.

[11] T. C. Waddington, Advan. Inorg. Chem. Radiochem. **1**, 157 (1959).

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

[13] Q. C. Johnson and D. H. Templeton, J. Chem. Phys. **34**, 2004 (1961).

[14] P. Hartmann, Acta Cryst. **11**, 365 (1958).

[15] F. Bertaut, J. Phys. Radium **13**, 499 (1952).

[16] R. E. Jones and D. H. Templeton, J. Chem. Phys. **25**, 1062 (1956).

TABLE. III. Values of the Madelung constants, on the basis of the Bertaut method, for nine ideal structures of $A^{+2}X_2^{-1}$ components as defined in the text. The charge distribution of the ion at position $\mathbf{r}_j$ is taken as $\sigma_j = a(|\mathbf{r}-\mathbf{r}_j|)^p$, with $p=0$, 1, 2, and 3, respectively.

Structure	$p=0$	$p=1$	$p=2$	$p=3$
fluorite	5.03947	5.03881	5.03879	5.03884
rutile I	4.78350	4.78307	4.78306	4.78308
rutile II	4.76067	4.76001	4.76000	4.76005
anatase	4.65310	4.65243	4.65242	4.65247
cadmium chloride	4.36953	4.36894	4.36893	4.36899
cadmium iodide	4.36632	4.36518	4.36516	4.36535
β-cristobalite	4.45506	4.45345	4.45342	4.45372
cuprite	4.44316	4.44250	4.44248	4.44254
β-quartz	4.40501	4.40311	4.40308	4.40350

spectively; i.e., the same distributions as employed by Johnson and Templeton. The results are given in Table III; all values refer to a composition $A^{+2}X_2^{-1}$. The values for cadmium chloride, cadmium iodide, anatase, rutile I, and rutile II refer to the ideal structures as defined in the Sec. I; for the β-quartz lattice $c/a=1.1$, $u=0.197$. The β-cristobalite structure is the high-temperature modification defined by Wyckoff.[9] All calculations were carried out on an IBM 1620 computer.

From the values of Table III we draw the following conclusions: (a) different forms for $\sigma_j(|\mathbf{r}-\mathbf{r}_j|)$ yield very nearly the same values for the Madelung constants; (b) in first approximation, the Madelung constant of a structure is determined by its coordination and decreases with decreasing coordination. The only exception is formed by the cadmium iodide and cadmium chloride lattices, which have abnormally low Madelung constants. (c) The values for the Madelung constants of the *ideal* cadmium iodide ($C6$) and cadmium chloride ($C19$) structures *are practically identical* (difference of the order of one-tenth of 1%).

Some of the values of Table III can be compared directly with those given by Johnson and Templeton,[13] as they refer to the same structures. These authors report for fluorite a value of 5.03879, for cuprite 4.44249, and for β-quartz 4.40225. It is of interest to note that the ideal and mineral forms of cadmium chloride differ by as much as 2% in their Madelung constants, the nonideal lattice having the larger value. As a comparison, it is found found that the nonideal types of cadmium iodide[13] differ from the ideal structure by only 0.2 of 1% in Madelung constant. Apparently, distortion results in a considerably more negative value for the Madelung energy *only* for the cadmium chloride lattice.

We observe, also, that the Madelung constant for the fluorite structure is much larger than for any of the other lattices; the smallest difference is of the order of 5% (with rutile I), much larger than that between $B2$ (cesium chloride) and $B1$ (sodium chloride), for example, which amounts to only 1%. In addition, we note that the Madelung constants of the cadmium iodide ($C6$) and cadmium chloride ($C19$) lattices are so low that their observed stability must be ascribed to additional contributions to the electrostatic component of the lattice energy (polarization effects).

B. Polarization Energy

As we have seen above, the Madelung constants for the $C6$ (cadmium iodide) and $C19$ (cadmium chloride) lattices are low with respect to other configurations of the same or lower coordination. On the other hand, these structures are very frequently observed with solids of AX_2 compounds where X is the larger ion. Apparently, their stability must be enhanced by an additional, considerable, electrostatic component of the lattice energy; this component is called "polarization energy"; it is of second order in perturbation theory. An estimate of this polarization energy can be obtained by calculating, from a Born-Haber cycle, the value of the crystal energy for several compounds with $C6$ or $C19$ structure. To a good approximation, it is found that the crystal energy is 1.05 times the Madelung energy. Compared with a Born-Mayer model without polarization components, this means an increase of 15 to 20% in lattice energy. This energy increase must be primarily due to a dipole polarization contribution, which is of the form $-\frac{1}{2}\alpha F_{\mathrm{el}}^2$ per X ion, where $\mathbf{F}_{\mathrm{el}}$ is the electric field strength at the X ion due to all the other charge distributions in the crystal (the field is identically zero at the site of an A ion). The electrostatic energy in first order (Madelung energy) is calculated on the basis of a model of *nonoverlapping* charge distributions. For this reason, we cannot use for the parameter α in the expression $-\frac{1}{2}\alpha F_{\mathrm{el}}^2$ the values of *free-ion* polarizabilities. Instead, we assume only the same *analytical form* for the polarization energy and determine α in the Born-Mayer model, using the Born-Haber values for the crystal energy of the stable structure. We will discuss this procedure in more detail later.

For the calculation of the total field strength $\mathbf{F}_{\mathrm{el}}$ at the site of an X ion, we choose the origin of our coordinate system at the site of the ion considered and denote the position vectors of the other ions by $\{\mathbf{r}_j\}$, their charges by $\{q_j\}$. The charge density $\rho(\mathbf{r})$, at position $\mathbf{r}$ is in the point-charge approximation, with V the volume of the unit cell,

$$\rho(\mathbf{r}) = \sum_j q_j \delta(|\mathbf{r}-\mathbf{r}_j|) = V^{-1} \sum_{\mathbf{h}} F(\mathbf{h}) \exp(-2\pi i \mathbf{h}\cdot\mathbf{r}),$$

where the Fourier coefficients (structure factors) $F(\mathbf{h})$ are given by

$$F(\mathbf{h}) = \int \rho(\mathbf{r}) \exp(2\pi i \mathbf{h}\cdot\mathbf{r}) d^3r = \sum\nolimits_l q_l \exp(2\pi i \mathbf{h}\cdot\mathbf{r}_l). \qquad (2)$$

Here, the summation over l extends over all ions of the unit cell of the crystal; $\mathbf{h}$ is a general vector of the reciprocal lattice.

Instead of the point charges, Bertaut[15] introduced spherical charge distributions $\sigma_j(|\mathbf{r}-\mathbf{r}_j|)$ centered at the ion positions $\mathbf{r}_j$, each normalized to unity. If we denote by $\sigma(\mathbf{r})$ the sum $\sum_j \sigma_j(|\mathbf{r}-\mathbf{r}_j|)$ over these distributions, then we can develop $\sigma(\mathbf{r})$ again as a Fourier series, with coefficients $\varphi(\mathbf{h})$ given by

$$\varphi(\mathbf{h})=\int_V \sigma(\mathbf{r})\exp(2\pi i\mathbf{h}\cdot\mathbf{r})d^3r.$$

The modified charge density function $\rho'(\mathbf{r})$ can then be written as

$$\rho'(\mathbf{r})=\sum_j q_j\sigma_j(|\mathbf{r}-\mathbf{r}_j|)=\int\rho(\mathbf{r}-\mathbf{u})\sigma(\mathbf{u})d^3u$$
$$=V^{-1}\sum_{\mathbf{h}} F(\mathbf{h})\varphi(\mathbf{h})\exp(-2\pi i\mathbf{h}\cdot\mathbf{r}). \tag{3}$$

The electric field strength $\mathbf{F}_{\text{el}}$ at the position $\mathbf{r}=0$ of the selected ion is given, using $\rho'(\mathbf{r})$ as charge density, by

$$\mathbf{F}_{\text{el}}(0)=\int\rho'(\mathbf{r})\nabla(1/r)d^3r=-\int[(\nabla\rho'(\mathbf{r}))/r]d^3r,$$

which, on substituting (3), becomes

$$\mathbf{F}_{\text{el}}(0)=\frac{2\pi i}{V}\sum_{\mathbf{h}} F(\mathbf{h})\varphi(\mathbf{h})\mathbf{h}\int[\exp(-2\pi i\mathbf{h}\cdot\mathbf{r})/r]d^3r$$
$$=\frac{2i}{V}\sum_{\mathbf{h}} F(\mathbf{h})\varphi(\mathbf{h})\mathbf{h}/h^2, \tag{4}$$

where we have used the identity[15]

$$\int[\exp(-2\pi i\mathbf{h}\cdot\mathbf{r})/r]d^3r=1/\pi h^2.$$

In combination with the expression (2) for $F(\mathbf{h})$ we then obtain the following final equation for the electric field strength at the selected site $r=0$,

$$\mathbf{F}_{\text{el}}(0)=-\frac{2}{V}\sum_{\mathbf{h}}\Big[\sum_l q_l\sin(2\pi\mathbf{h}\cdot\mathbf{r}_l)\Big]\varphi(\mathbf{h})\mathbf{h}/h^2. \tag{5}$$

In this expression, the summation in l extends over the unit cell of the crystal and the summation in $\mathbf{h}$ over the reciprocal lattice. The Fourier coefficients $\varphi(\mathbf{h})$ depend, of course, on the analytic form of the distribution functions $\sigma_j(|\mathbf{r}-\mathbf{r}_j|)$; in all cases $\varphi(\mathbf{h})$ is real, with the property $\varphi(-\mathbf{h})=\varphi(\mathbf{h})$. It is verified directly from (5) that $\mathbf{F}_{\text{el}}$ is identically zero if the ion considered is located at a center of symmetry of the crystal. Values of $\varphi(\mathbf{h})$, for σ_j of the form $a(|\mathbf{r}-\mathbf{r}_j|)^p$ with $p=0$, 1, 2, and 3, were calculated by Jones and Templeton[16]; in our analysis of the polarization energy we have used the same charge distributions. On the basis of (5) it is most convenient to calculate the components of $\mathbf{F}_{\text{el}}$ along the basis vectors $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ of the reciprocal lattice for each structure; we denote these components by F_1, F_2, and F_3, respectively.

TABLE IV. Values of the parameter K in the dipole-polarization energy $E_{\text{pol}}=-(\alpha/R^4)K$ for nine different structures of AX_2 compounds, with α in units 10^{-24} cm^3, R in Å, and E_{pol} in kcal/mole; the cation has charge two. The last column gives the symmetry properties of the electric field components F_1, F_2, F_3 along the axes $\mathbf{b}_1$, $\mathbf{b}_2$, $\mathbf{b}_3$ of the reciprocal lattice.

Structure	K	Field components
fluorite	0	$F_1=F_2=F_3=0$
rutile I	32	$F_1=F_2$, $F_3=0$
rutile II	67	$F_1=F_2$, $F_3=0$
anatase	425	$F_1=F_2=0$, F_3
cadmium chloride	2391	$F_1=F_2=F_3$
cadmium iodide	2419	$F_1=-F_2=0$, F_3
β-cristobalite	0	$F_1=F_2=F_3=0$
cuprite	0	$F_1=F_2=F_3=0$
β-quartz	8	$F_1=-F_2$, $F_3=0$

For all (ideal) structures of AX_2 compounds the electric field at the site of an A ion is identically zero, so that only the polarization energy of X ions remains to be calculated. The total polarization energy, for one mole of the compound AX_2, can be written in the form

$$E_{\text{pol}}=-(\alpha/R^4)K, \tag{6}$$

where α is a polarization parameter associated with the X ion, R is the distance between nearest neighbors in the lattice, and where the parameter K is a function only of the type of structure. In Table IV average values of K (averaged for $p=1$, 2, and 3) are given for nine different (ideal) structures, with E_{pol} in kcal/mole, α in units 10^{-24} cm^3, and R in units 10^{-8} cm. Also listed are the symmetry properties of the three components F_1, F_2, F_3 of the electric field along the basis vectors of the respective reciprocal lattices. It is seen from Table IV that the polarization energy in the cadmium iodide ($C6$) and cadmium chloride ($C19$) structures is much larger than in the other seven configurations. The relative difference between $C6$ and $C19$, for the same nearest-neighbor distance R, is small, namely, only of the order of 1% and in favor of cadmium iodide. As we will see later, this difference is negligible compared to that between the three-ion energies in the two structures for relatively *small* values of βR. When, on the other hand, βR is larger than about 1.3, the three-ion energies are very nearly the same and the 1% higher polarization energy for $C6$ is overcompensated by a gain in Madelung energy which the $C19$ structure can acquire through distortion of the ideal lattice.

IV. THREE-ION INTERACTION ENERGY

The evaluation of three-ion interactions for solids of AX_2 compounds follows closely the analysis given in [I], [II], and [III] for rare-gas crystals and ionic solids of composition AX. We select a central ion a and consider all triplets (abc) formed by that ion and two other ions of the crystal. As before, we consider only isosceles triangles, i.e., b and c are ions from the same shell around the central ion a. The three-ion interactions are determined in first and second orders of perturbation theory; the zero-order wave function for the triplet (*abc*) is (Slater determinant)

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

where 1, 2, 3 number the electrons, with one (effective) electron per ion. The wave function for ion *a* is

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

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

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

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

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

in terms of the perturbations for the pairs.

We denote by E_1 and E_2 the first- and second-order perturbation energies for the triplet, by $E_1{}^{(0)}$ and $E_2{}^{(0)}$ the corresponding sums of interactions for the *isolated* pairs, and by $\Delta E_1/E_1{}^{(0)}=(E_1-E_1{}^{(0)})/E_1{}^{(0)}$ and $\Delta E_2/E_2{}^{(0)}=(E_2-E_2{}^{(0)})/E_2{}^{(0)}$ the relative first- and second-order three-ion interactions. In view of the exchange character of the three-ion forces, only triangles of small dimensions need be considered. If the ions of the triplet are of the same kind (A or X), then the following approximate equality holds

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

for all values of the opening Θ of the triangle at the central ion. If the ions of the triplet are of both types (A and X), then this equality is again valid if the Gaussian parameters β and β' are about equal, i.e., for values of γ not much larger than 1. If $\gamma\gg1$, then we consider only triplets of the larger ions, and (7) holds again. For the total three-ion energy, $\Delta E=\Delta E_1+\Delta E_2$, of the triplet, relative to the total pair energy $E^{(0)}=E_1{}^{(0)}+E_2{}^{(0)}$, we can then write, in view of (7),

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

so that

$$\Delta E\approx(\Delta E_1/E_1{}^{(0)})E^{(0)}, \tag{8}$$

for each (isosceles) triangle and $\gamma\sim1$.

It has been found ([I], [II]) that $\Delta E_1/E_1{}^{(0)}$ (or $\Delta E_2/E_2{}^{(0)}$), is <0 for values of the opening angle Θ between 60° and approximately 110°, and positive for larger Θ. The relative three-ion interactions amount to about -20% at $\Theta=60°$; they are generally smaller at $\Theta=180°$ except for the smallest values of $\beta R(<1.1)$. For stability calculations it is appropriate to write the pair energy $E^{(0)}$ in (8) for each triplet as a sum of a repulsive term $E_{\mathrm{rep}}{}^{(0)}$ and an attractive term $E_{\mathrm{attr}}{}^{(0)}$; $E_{\mathrm{rep}}{}^{(0)}$ combines $E_1{}^{(0)}$ and the second-order exchange interactions for the pairs, whereas $E_{\mathrm{attr}}{}^{(0)}$ is the long-range van der Waals component (without exchange). In this way it is possible to identify $E_{\mathrm{rep}}{}^{(0)}$ with the short-range pair repulsion of the Born-Mayer model. On this basis, Eq. (8) for ΔE becomes, for each triplet,

$$\Delta E\approx(\Delta E_1/E_1{}^{(0)})E_{\mathrm{rep}}{}^{(0)}(1+E_{\mathrm{attr}}{}^{(0)}/E_{\mathrm{rep}}{}^{(0)}), \tag{9}$$

in which form we use it for the stability analysis.

Consider a central ion and a selected shell of ions around it. For all triplets with two ions from that shell, the quantities $E_{\mathrm{rep}}{}^{(0)}$ and $E_{\mathrm{attr}}{}^{(0)}$ are practically constant, so that we can associate with a given *shell* certain values of $E_{\mathrm{rep}}{}^{(0)}$ and of $(1+E_{\mathrm{attr}}{}^{(0)}/E_{\mathrm{rep}}{}^{(0)})$. If the latter factor is <0 for the shell, which is the case if an ion from the shell and the central ion attract each other, then ΔE for each triplet has the opposite sign from that of $\Delta E_1/E_1{}^{(0)}$ of the triplet. If an ion from the shell and the central ion repel each other, then the factor $(1+E_{\mathrm{attr}}{}^{(0)}/E_{\mathrm{rep}}{}^{(0)})$ is >0, so that ΔE and $\Delta E_1/E_1{}^{(0)}$ have the same sign. From the properties of $\Delta E_1/E_1{}^{(0)}$, as a function of Θ, we see that three-ion interactions from the selected shell in the first case favor the crystal structure with the largest number of triangles of *large* opening, in the second case the structure with the largest number of triangles of *small* opening .

For the determination of the total three-ion component of the static lattice energy of AX_2 compounds we must know the triplet arrangements in the different structures for a number of shells close to the central ion, once for A as central ion and once for X at the center of the triangles. The number of shells which must be considered depends on βR (R is the nearest-neighbor distance), on the specific structure, and on $\gamma=(\beta'/\beta)^2$. For $\gamma\gg1$ it is sufficient to know the triplets $A_0A_nA_n$ or $X_0X_nX_n$ (depending on which ion is larger); the subscript "0" refers to the central ion, and n numbers the shell of A ions, or X ions, respectively. We have

TABLE V. Numbers of ion pairs and of triplets $A_0X_1X_1$ involving a central ion A and its first shell of neighbors for the nine ideal structures of AX_2 compounds. The opening of the triangle at the central ion is denoted by Θ.

Structure	Number of pairs	Number of triplets $A_0X_1X_1$	$\cos\Theta$
fluorite	8	12	+0.3333
		12	−0.3333
		4	−1.0000
rutile I	6	2	+0.5000
		8	0.0000
		2	−0.5000
		3	−1.0000
rutile II	6	12	0.0000
		3	−1.0000
anatase	6	12	0.0000
		3	−1.0000
cadmium chloride	6	12	0.0000
		3	−1.0000
cadmium iodide	6	12	0.0000
		3	−1.0000
β-cristobalite	4	6	−0.3333
cuprite	4	6	−0.3333
β-quartz	4	6	−0.3333

TABLE VI. Numbers of ion pairs and of triplets $X_0A_1A_1$ involving a central ion X and its first shell of neighbors, for the nine ideal structures of AX_2 compounds. The opening of the triangle at the central ion is denoted by Θ.

Structure	Numbers of pairs	Number of triplets $X_0A_1A_1$	$\cos\Theta$
fluorite	4	6	−0.3333
rutile I	3	3	−0.5000
rutile II	3	1	0.0000
		2	−0.7071
anatase	3	2	0.0000
		1	−1.0000
cadmium chloride	3	3	0.0000
cadmium iodide	3	3	0.0000
β-cristobalite	2	1	−1.0000
cuprite	2	1	−1.0000
β-quartz	2	1	−0.9107

analyzed the nine different structures in terms of their triplet arrangements relevant for the three-ion crystal energy, as a function of βR and of γ. Detailed results will not be given here, but it is of interest to consider in advance a few illustrative examples from which certain conclusions can already be drawn.

Suppose first that βR is relatively large and γ small, i.e., that the first shell of ions around a central ion gives an essential contribution to the three-ion energy. The corresponding triplets can be of the form $(A_0X_1X_1)$ or of the form $(X_0A_1A_1)$; in the first case, an A ion is at the center of the triplets and in the second case X is the central ion. In Tables V and VI we list these triplets for the nine different lattice types.

Upon inspection of the tables it appears that the arrangement of $A_0X_1X_1$ triplets in fluorite ($C1$) is the same as in cesium chloride ($B2$); in rutile II ($C4$), anatase ($C5$), cadmium iodide ($C6$), and cadmium chloride ($C19$) the same as in sodium chloride ($B1$); in rutile I ($C4$) the arrangement is only slightly different from that in $B1$ and in the structures with 4,2-coordination ($C3$, $C8$, $C9$) we have sphalerite ($B3$), wurtzite ($B4$) arrangements. In other words, the effect of these triplets on stability is the same as in the lattice types for AX compounds, analyzed in [II] and [III], where we found that these triplets favor the $B2$ configuration. Therefore, the fluorite structure is the most stable one for AX_2 compounds (large βR, small γ), and at large values of βR no other triangles with A as the central ion need be considered. The $X_0A_1A_1$ triplets (Table VI) are much less important in number; therefore, we expect qualitatively that three-ion interactions at large values of βR will stabilize the fluorite structure. When βR decreases, γ increases and, consequently, the importance of $A_0X_1X_1$ ($X_0A_1A_1$) triplets diminishes, just as in the transition from $B2$ to $B1$ stability. The difference here is that, if A is the larger ion, then γ increases more slowly than for AX composition, resisting a lowering of the coordination for solids of these AX_2 compounds. In addition, the Madelung energy of the fluorite lattice is relatively much larger than that of the other configurations; this difference is never overtaken, even for the smallest values of βR, if A is the larger ion.

As a second example, we discuss qualitatively the *relative stability* of the cadmium iodide ($C6$) and cadmium chloride ($C19$) structures. As we found before, these two lattices are practically identical with respect to their electrostatic energies; also the non-Coulombic repulsions are very nearly the same. These structures are frequently observed with AX_2 compounds where X is the larger ion and where γ is relatively large. As a consequence, we must primarily consider triplets $X_0X_nX_n$ and determine the effect of these three-ion interactions on stability.

The X ions in these two structures have *close-packed configurations*, as the atoms in rare-gas crystals: hexagonal close-packed in $C6$, face-centered cubic in $C19$. We found in [I] for rare-gas crystals that only differences in three-atom energies between the shells of nearest neighbors have to be considered, in view of the large values of βR for these solids ($\geqslant 2$). For ionic solids these differences are negligible on the energy scale of their cohesive energies. In addition, the βR values are now much smaller, so that we cannot limit ourselves to the first shell of X ions.

The important shells for stability appear to be (as shown in a later section) the fourth shell of X ions in $C6$ and the third shell of X ions in $C19$, both at a distance $6^{1/2}R$ from the central ion. These shells give rise to a negative first-order three-ion energy ΔE_1, considerably more negative in $C19$ than in $C6$ at small values of $\beta R(<1.3)$. As these shells are clearly in the attractive field of the central ion, their weighting factors are <0, and the resulting three-ion energy is repulsive, more repulsive in $C19$ than in $C6$. Consequently, the $C6$ (cadmium iodide) structure is the more stable of the two at small values of βR, in agreement with experiment. For values of $\beta R>1.3$ these critical shells are less important, and stability shifts towards the $C19$ lattice probably because distortion of this lattice results in a lower Madelung energy.

V. CRYSTAL STABILITY OF AX_2 COMPOUNDS

We now present the results of the stability analysis for solids of AX_2 compounds, comparing the static lattice energies of the nine (ideal) structures defined earlier. Each solid is characterized by the Gaussian parameters $\gamma=(\beta'/\beta)^2$ and βR (β represents the larger ion), and by the type of ion (A or X) associated with β.

The static lattice energy E_{st} for each structure and for one mole of the compound AX_2 is written as

$$E_{\mathrm{st}}=E_{\mathrm{M}}+E_{\mathrm{p.r.}}+\sum_{a<b<c}\Delta E(abc)+E_{\mathrm{pol}}, \qquad (10)$$

where E_{M} stands for the Madelung energy, $E_{\mathrm{p.r.}}$ for total non-Coulombic pair repulsion, $\Delta E(abc)$ for the (first- plus second-order) three-ion interaction of the triplet (*abc*), and E_{pol} for the (dipole) polarization energy $-(\alpha/R^4)K$ of the lattice.

We compare the static lattice energies for the nine structures at the *observed* value R of the nearest-neighbor distance in the stable structure. Let α_1 denote the pair repulsion between nearest neighbors at the equlibrium distance R. The pair repulsion between more distant ions is calculated relative to that between nearest neighbors by assuming that this ratio is equal to that for first-order interactions between Gaussian distributions of charge. Since these interactions are γ-dependent, we thereby take into account *the different size of A and X ions*. The total pair repulsion $E_{\text{p.r.}}$ of (10) can in this way be expressed as a function of α_1, for each structure.

Also the three-ion energy ΔE of (10) can be written as a function of α_1 and of the lattice considered. To see this, we note that in each term $\Delta E(abc)$ there again occurs, according to (9), the non-Coulombic pair repulsion $E_{\text{rep}}^{(0)}$. For each triplet, therefore, this term can be related to the pair repulsion α_1 between nearest neighbors. By determining the values of the parameter $(1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)})$ of (9) for each different shell (as specified later), we express the total three-ion energy for each lattice as a function of α_1.

The values for this nearest-neighbor repulsion α_1, at the observed equilibrium separation R, are determined from information on the *stable structure*, on the basis of the following considerations. We distinguish between two possibilities: (a) for the stable structure the polarization parameter K is *zero or negligibly small*, i.e., E_{pol} may be omitted from (10) for this particular structure; (b) K for the stable structure is *large* ($C6$ or $C19$). Category (a) comprises all compounds where A is the larger ion, since here the stable structure is always $C1$. Certain compounds where X is the larger ion also belong in this class, namely (Table II) the oxides of Si, Ti, Zr, and Hf, as well as $SrCl_2$. For this category we can, in principle, *not* determine the stability of $C6$ and $C19$ *with respect to* the other structures, since no reliable estimates of E_{pol} can be made in this case (except if A is the larger ion and γ is large). For both categories (a) and (b) we make a further distinction, according to whether or not the static lattice energy of the stable structure is known from a Born-Haber cycle (determined from thermochemical data and electron affinities).

We now have to consider four different possibilities:

(*a1*) *$E_{pol}\sim 0$; Born-Haber values known.* We substitute the Born-Haber value for the static lattice energy on the left-hand side of (10), which equation is then solved for α_1. The values of E_{st} for the other structures (generally, excluding $C6$ and $C19$) are determined at the same value of βR. The lattice with the largest negative E_{st} is the most stable one at R. The result is correct if this is just the observed structure.

(*a2*) *$E_{pol}\sim 0$; Born-Haber values not known.* The nearest-neighbor pair repulsion α_1 can in this case not be determined from (10) in a one-step procedure. We now adopt validity of the Born-Mayer model with an *effective* pair repulsion varying with distance as R^{-p}. The static lattice energy of the observed structure, at equlibrium distance R, is then given by

$$E_{\text{st}}=E_{\text{M}}(1-1/p). \tag{11}$$

Different values for p (between $p=7$ and $p=12$) are then chosen, and the corresponding values of E_{st} calculated from (11). With this set of values we obtain, from (10), a set of values for α_1, with which we proceed as under (a1). This method of determining α_1 via (11), for a range of values of p, is also in (a1) preferable to using the Born-Haber values directly, since, for example, the electron affinities of the ions of O, S, Se, and Te are not known with sufficient accuracy.

(*b1*) *E_{pol} large; Born-Haber values known.* Category (b) refers to the $C6$ and $C19$ structures exclusively. In this case we cannot determine α_1 directly from (10), since this equation contains E_{pol} of which we know only that its contribution to the crystal energy is appreciable. We therefore extend the Born-Mayer model by also incorporating E_{pol} in the expression for the static lattice energy (which contains the Madelung energy and the total effective pair repulsion). Since E_{pol} varies with R as R^{-4}, it follows readily that the expression for the static lattice energy of the stable structure, at the observed nearest-neighbor distance R, is now given by

$$E_{\text{st}}=E_{\text{M}}(1-1/p)+[(p-4)/p]E_{\text{pol}}, \tag{12}$$

where p denotes again the exponent in the dependence R^{-p} of the effective repulsion on distance.

Using the Born-Haber value for E_{st} we obtain, from (12), E_{pol} as a function of p. Then, substituting E_{pol} into (10), we determine α_1 as a function of p, and complete the calculation of E_{st} for the remaining eight structures.

(*b2*) *E_{pol} large; Born-Haber values not known.* Here, the unknowns in Eq. (10) are E_{st}, α_1, and E_{pol}. We determine E_{st} by observing that for several compounds of category (b1) a relation $E_{\text{st}}\sim 1.05E_{\text{M}}$ holds to a good approximation. This applies for the compounds TiS_2, $MgCl_2$, $MgBr_2$, MgI_2, and CaI_2; from thermochemical data[17] and electron affinities we determined Born-Haber values and obtained for $E_{\text{st}}/E_{\text{M}}$ (in order of the compounds as given above) the values 1.05, 1.04, 1.06, 1.10, and 1.07. The same relation is assumed to hold for all compounds of class (b2); we then calculate again E_{pol} for different values of p and proceed as before.

It is noted that the *relative* stability of the $C6$ and C19 configurations is not affected by an uncertainty concerning the values of E_{pol}, since these values can be assumed to be practically the same in the two structures.

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[17] O. Kubaschewski and E. L. Evans, *Metallurgical Thermochemistry* (Pergamon Press Ltd., London, 1956), Chap. 4.

TABLE VII. Madelung energy E_M (kcal/mole), total pair repulsion $E_{p.r.}$, total three-ion energies for triplets $A_0X_1X_1$ ($X_0A_1A_1$), triplets $X_0X_nX_n$, $A_0A_mA_m$, and the sum of two-body and three-body energies (all in units of nearest-neighbor repulsion) for CaF_2, Na_2O, and Li_2Se. The last three columns list the difference in energy δE between the corresponding structure and the fluorite configuration (in kcal/mole); the values in parentheses refer to pair interactions only.

CaF_2; $\beta R=1.985$, $\gamma=1.244$

								δE	
Structure	E_M	$E_{p.r.}$	$A_0X_1X_1+X_0A_1A_1$	$A_0A_1A_1$	$X_0X_1X_1$	$E_{p.r.}+\Delta E$	$p=8$	$p=9$	$p=10$
*C*1	−706.9	9.3613	−1.4685	···	−0.0836	7.8092	0	0	0
*C*4-I	−671.1	6.7400	−0.3572	···	0.2103	6.5931	22.0(11.0)	23.6(13.8)	24.8(16.0)
*C*4-II	−668.1	6.0718	−0.4859	−0.0025	0.1433	5.7267	15.2(7.7)	17.9(11.2)	19.9(14.0)
*C*5[a]	−655.0	6.1437	−0.4314	0.0027	0.1688	5.8838	30.1(21.5)	32.5(24.9)	34.5(27.6)
*C*19[a]	−626.3	6.2155	−0.7700	0.0700	0.1688	5.6843	56.7(50.9)	59.2(54.2)	61.4(56.8)
*C*6[a]	−625.9	6.2155	−0.7700	0.0700	0.1690	5.6845	57.0(51.3)	59.6(54.6)	61.8(57.2)
*C*9	−624.7	4.0000	0.3724	···	···	4.3724	43.3(31.6)	47.6(37.2)	51.1(41.7)
*C*3	−623.2	4.0000	0.3724	···	···	4.3724	44.8(33.1)	49.1(38.7)	52.6(43.2)

Na_2O; $\beta R=1.44$, $\gamma=3.75$

							δE	
Structure	E_M	$E_{p.r.}$	$A_0X_1X_1+X_0A_1A_1$	$\sum_m A_0A_mA_m$	$E_{p.r.}+\Delta E$	$p=8$	$p=9$	$p=10$
*C*1	−696.8	9.9027	−0.6113	−0.3157	8.9757	0	0	0
*C*4-I	−661.6	7.2236	0.1225	0.6624	8.0085	25.9(11.7)	27.0(14.3)	27.8(16.4)
*C*4-II	−658.5	7.2803	0.1018	0.6063	7.9884	28.7(15.2)	29.8(17.8)	30.6(19.8)
*C*5[a]	−644.5	7.8123	0.0997	0.0140	7.9260	42.1(33.9)	43.2(36.0)	44.2(37.6)
*C*19[a]	−610.8	8.5477	−0.2944	−0.0328	8.2205	78.7(74.1)	79.5(75.4)	80.1(76.4)
*C*6[a]	−610.4	8.5384	−0.2944	−0.0328	8.2112	79.0(74.4)	79.8(75.7)	80.5(76.8)
*C*9	−615.8	4.0728	0.5474	−0.0012	4.6190	38.7(29.7)	43.3(35.4)	47.2(40.0)
*C*3	−614.4	4.1886	0.5474	0.1241	4.8601	42.5(32.1)	46.9(37.7)	50.4(42.2)

Li_2Se; $\beta R=1.056$, $\gamma=41$

							δE	
Structure	E_M	$E_{p.r.}$	$A_0X_1X_1+X_0A_1A_1$	$\sum_m A_0A_mA_m$	$E_{p.r.}+\Delta E$	$p=8$	$p=9$	$p=10$
*C*1	−643.2	62.8067	−3.1436	−2.8642	56.7989	0	0	0
*C*4-I	−610.6	43.2606	−1.3676	−4.1798	37.7132	5.6(7.6)	8.6(10.4)	11.0(12.6)
*C*4-II	−607.7	42.0195	−1.5820	−0.7294	39.7081	11.3(8.9)	14.0(11.8)	16.1(14.2)
*C*5[a]	−594.0	46.3850	−1.6098	15.5910	60.3662	54.2(28.2)	53.7(30.5)	53.2(32.4)
*C*19[a]	−558.1	54.3045	−1.9871	12.2363	64.5537	96.1(74.2)	94.9(75.4)	93.9(76.4)
*C*6[a]	−557.7	54.3585	−1.9871	11.6987	64.0701	95.8(74.7)	94.6(75.9)	93.7(76.8)
*C*9	−568.5	9.7382	−0.2753	0.1137	9.5766	7.9(6.8)	15.3(14.3)	21.2(20.4)
*C*3	−567.1	19.0216	−0.2753	−2.1545	16.5918	19.2(20.0)	25.5(26.3)	30.6(31.3)

[a] The polarization energy is not included.

For the presentation of numerical results, we distinguish between the following three classes of solids:

(I) *A* is the larger ion (*C*1 stability);
(II) *X* is the larger ion; no polarization energy in the stable structure (*C*1, *C*4, *C*8, and *C*9 stability);
(III) *X* is the larger ion; stable structure *C*6 or *C*19.

It is of importance to also include in the results the stability relations obtained on the basis of (non-Coulombic) *pair interactions*, i.e., by omitting from Eq. (10) the contribution of three-ion forces to the lattice energy. This comparison is relevant, since a Born-Mayer type of pair potential, *extended* by taking into account the difference in size between *A* and *X* ions through the parameter γ, for each compound, is expected to yield stability relations closely similar to those of the Goldschmidt rules.

Class (I). Detailed numerical results are given for three typical representatives of this class: CaF_2 ($\beta R=1.99$, $\gamma=1.24$), Na_2O ($\beta R=1.44$, $\gamma=3.75$), and Li_2Se ($\beta R=1.06$, $\gamma=41$). In Table VII we list, for these three compounds in the nine ideal structures, the Madelung energy (in kcal/mole), the total pair repulsion $E_{p.r.}$ (in units of nearest-neighbor repulsion), the three-ion energy for triplets $A_0X_1X_1$ ($X_0A_1A_1$), triplets $X_0X_nX_n$ (summed over *n*), $A_0A_mA_m$ (summed over *m*), as well as the sum of pair- and three-ion interactions. The summations over *n* and *m* extend up to values of βR_n, βR_m of about 3.4 (for larger values three-ion energies are negligible.) The last three columns of the table give, in kcal/mole, the difference in lattice energy δE between the structure considered and the stable *C*1 configuration, for values $p=8$, 9, and 10 of the exponent *p* in the Born-Mayer effective pair repulsion R^{-p}. A positive value means that *C*1 is the most stable structure. The weighting factors $(1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)})$ for the different shells are the same as those used in the analysis of alkali halide crystals and of solids of II-VI and III-V compounds (a two-step function with values 0.5, 0.25 for shells in the repulsive part of the pair potential, and a value −1 for shells in the attractive part of the pair potential). We also list in the last three columns, in parentheses, the difference in lattice energy between the corresponding structure and *C*1, calculated on the basis of *pair interactions* alone.

TABLE VIII. Madelung energy E_M (kcal/mole), total pair repulsion $E_{\mathrm{p.r.}}$, total (first- plus second-order) three-ion energies for triplets $A_0X_1X_1$ ($X_0A_1A_1$), $X_0X_nX_n$, and sum of two-body and three-body energies (all in units of nearest-neighbor repulsion), for $SrCl_2$, ZrO_2, and HfO_2. The last three columns list the difference in energy δE between the corresponding structure and the fluorite configuration (in kcal/mole); values in parentheses refer to pair interactions only.

$SrCl_2$; $\beta R=1.686$, $\gamma=1.416$

							δE	
Structure	E_M	$E_{\mathrm{p.r.}}$	$A_0X_1X_1+X_0A_1A_1$	$\sum_n X_0X_nX_n$	$E_{\mathrm{p.r.}}+\Delta E$	$p=8$	$p=9$	$p=10$
$C1$	−553.7	12.7335	−2.9293	−0.5572	9.2470	0	0	0
$C4$-I	−525.7	9.2947	−1.1169	1.8368	10.0146	33.7(9.3)	33.1(11.4)	32.6(13.0)
$C4$-II	−523.1	8.1073	−1.4427	1.4096	8.0742	21.8(5.8)	22.8(8.6)	23.6(10.9)
$C5$[a]	−511.3	8.3046	−1.4320	1.5345	8.4071	36.1(18.9)	36.8(21.6)	37.4(23.7)
$C19$[a]	−480.2	8.3404	−1.8795	1.5345	7.9954	64.1(50.1)	65.2(52.8)	66.0(54.9)
$C6$[a]	−479.7	8.3293	−1.8795	1.5407	7.9905	64.6(50.0)	65.6(52.7)	66.5(54.8)
$C9$	−489.4	4.2638	0.0329	0.0820	4.3787	27.9(18.9)	31.9(24.1)	35.1(28.2)
$C3$	−488.2	4.5275	0.0329	0.4172	4.9776	33.5(21.3)	37.1(26.3)	39.9(30.3)

ZrO_2; $\beta R=1.317$, $\gamma=2.2$

							δE	
Structure	E_M	$E_{\mathrm{p.r.}}$	$A_0X_1X_1+X_0A_1A_1$	$\sum_n X_0X_nX_n$	$E_{\mathrm{p.r.}}+\Delta E$	$p=8$	$p=9$	$p=10$
$C1$	−3048	18.5105	−4.3908	−2.5829	11.5386	0	0	0
$C4$-I	−2893	13.7291	−1.9059	−2.2248	9.5984	91(57)	98(68)	104(76)
$C4$-II	−2879	12.3500	−1.4073	−1.7287	9.2140	92(42)	101(56)	108(68)
$C5$[a]	−2814	12.7734	−3.7042	−1.7294	7.3389	95(116)	111(129)	123(140)
$C19$[a]	−2643	12.7372	−3.0443	−1.7294	7.9635	287(286)	300(299)	310(310)
$C6$[a]	−2640	12.7372	−3.0443	−1.6982	7.9947	291(289)	304(302)	314(313)
$C9$	−2694	5.3450	−1.3266	−0.0364	3.9820	105(83)	132(113)	154(137)
$C3$	−2687	6.8645	−1.3266	−0.4269	5.1110	149(121)	172(148)	191(169)

HfO_2; $\beta R=1.329$, $\gamma=1.54$

							δE	
Structure	E_M	$E_{\mathrm{p.r.}}$	$A_0X_1X_1+X_0A_1A_1$	$\sum_n X_0X_nX_n$	$E_{\mathrm{p.r.}}+\Delta E$	$p=8$	$p=9$	$p=10$
$C1$	−3020	15.7285	−3.8828	−1.8183	10.0274	0	0	0
$C4$-I	−2867	12.0835	−1.4812	−1.5720	9.0303	115(66)	120(75)	123(83)
$C4$-II	−2853	10.6854	−0.7598	−1.2141	8.7115	117(46)	123(59)	127(70)
$C5$[a]	−2789	11.1756	−1.9950	−1.2172	7.9634	153(122)	162(134)	169(144)
$C19$[a]	−2619	10.0651	−2.8248	−1.2172	7.0231	288(289)	300(302)	311(312)
$C6$[a]	−2616	11.1791	−2.8248	−1.1967	7.1567	296(294)	308(307)	318(317)
$C9$	−2669	4.2969	−0.0749	−0.0274	4.1946	131(76)	156(107)	175(132)
$C3$	−2663	6.0688	−0.0749	−0.2967	5.6972	194(125)	212(151)	227(172)

[a] The polarization energy is not included.

The values in Table VII for the structures $C5$ (anatase), $C6$ (cadmium iodide), and $C19$ (cadmium chloride) were calculated *without* taking polarization energy into account. Since the electric field at the site of the larger ion (A) is identically zero for this class of solids, polarization contributions from the smaller ion (X) are small. It is seen from the table that the fluorite structure is indeed always the most stable one, both on the basis of pair interactions and when three-ion energy is taken into account.

Class (*II*). In this class we find the compounds ZrO_2, HfO_2, $SrCl_2$ ($C1$ stability); MgF_2, TiO_2 ($C4$ stability); and SiO_2, BeF_2 ($C8$, $C9$ stability). The range of βR values extends from 1.86 (MgF_2) to 0.91 (SiO_2); the γ values extend from 2.17 to 15.4.

We first give the results for $SrCl_2$, ZrO_2, and HfO_2 ($C1$ stability). In Table VIII we list, for these three compounds, the same quantities as in Table VII; the values in parentheses in the last three columns refer again to a pair potential only (Madelung energy plus sum of non-Coulombic, γ-dependent pair repulsions).

We see from the table, that, for all three compounds, three-ion interactions *increase* $C1$ *stability*, in particular with respect to $C3$, $C4$, and $C9$, compared with the results based on pair interactions alone; this extra stability arises from triplets $A_0X_1X_1$ ($X_0A_1A_1$) and $X_0X_1X_1$. The effect of three-ion interactions is, therefore, to *resist* a lowering of the coordination number as long as γ is relatively small. In the case of alkali halides, on the other hand, the γ values are much larger for comparable values of βR; for this category of ionic solids the $B1$ structure (coordination 6) is, consequently, more stable than $B2$ (coordination 8). Although we have not taken account of polarization energy for the structures $C6$, $C19$, (and $C5$), it is seen from the table that the fluorite configuration is more stable than these structures by a large margin; this difference cannot be overtaken by polarization effects.

Next, we discuss MgF_2 ($\beta R=1.86$, $\gamma=2.17$) and TiO_2 ($\beta R=1.15$, $\gamma=4.18$), for which the observed stable structure is $C4$ (rutile type). Here, we have the unusual phenomenon that a structure is stable in two *widely separated domains* of βR values, for similar values of γ. In view of this peculiarity, the stability analysis requires a more precise consideration of the influence of three-ion interactions than for the solids discussed

TABLE IX. Total pair repulsion $E_{\text{p.r.}}$ and first-order three-ion energies ΔE_1 for triplets $A_0X_1X_1$ ($X_0A_1A_1$), $X_0X_1X_1$, and $X_0X_2X_2$, for MgF_2 in the structures $C1$, $C4$-I, $C4$-II, and $C9$. The quantities βR_1 and βR_2 denote the dimensionless distances from the first two shells of X ions in these structures to the central ion (X_0).

MgF_2; $\beta R=1.86$, $\gamma=2.17$

Structure	$E_{\text{p.r.}}$	$A_0X_1X_1$ $+X_0A_1A_1$	βR_1	$X_0X_1X_1$	βR_2	$X_0X_2X_2$
$C1$	15.2954	−7.7452	2.15	−2.5418	3.04	−0.3545
$C4$-I	10.4600	−3.5578	2.63	−2.2306	2.94	0.0023
$C4$-II	8.3755	−3.5130	2.63	−1.7428	3.22	0.00015
$C9$	4.1884	−0.5050	3.04	−0.0771		

TABLE X. Energy differences $\delta(C9\text{-}C4)$ between the cristobalite and rutile-II structures, and $\delta(C1\text{-}C4)$ between the fluorite and rutile-II structure (in kcal/mole), for MgF_2 as a function of weighting factors ($S1$,$S2$) for the first few shells of X ions, and of the exponent $p=8$, 9, and 10 of the effective Born-Mayer pair repulsion. The sets $S1$,$S2$ are defined in the text.

	$\delta(C9\text{-}C4)$			$\delta(C1\text{-}C4)$		
MgF_2	$p=8$	$p=9$	$p=10$	$p=8$	$p=9$	$p=10$
pair interactions	2.1	7.7	12.0	36.4	27.2	20.2
set $S1$	12.7	17.1	20.6	22.1	14.6	8.5
set $S2$	0	5.9	10.5	−5.3	−9.8	−13.4

so far. The principal structures to be compared for stability appear to be $C1$, $C4$-I, $C4$-II, and $C9$; with respect to these four configurations the remaining structures are found to be of much lower stability.

In Table IX we list, for the structures $C1$, $C4$-I, $C4$-II, and $C9$ of the compound MgF_2, the total pair repulsion $E_{\text{p.r.}}$ and the *first-order* three-ion energies ΔE_1 for triplets $A_0X_1X_1$ ($X_0A_1A_1$), $X_0X_1X_1$, and $X_0X_2X_2$. The corresponding dimensionless distances βR_1 and βR_2 for the first two shells of X ions are also given. First we note that three-ion interactions arising from triplets $A_0X_1X_1$ ($X_0A_1A_1$) are *attractive* in all four configurations (since the weighting factor for the shell of nearest neighbors is positive) and that they favor the *fluorite* structure.

The three-ion energy resulting from triplets $X_0X_1X_1$ has a *very sensitive effect* on crystal stability. The first shell of X ions is in $C1$ at distance $\beta R_1=2.15$, in $C4$-I, II at distance 2.62, and in $C9$ at distance 3.04. The weighting factor for this shell in $C9$ is certainly negative; we take it as −1, in accordance with the procedure adopted for all other ionic solids considered previously. To estimate the weighting factor for this shell in the fluorite and rutile structures, we note that the fluorine ion is isoelectronic with neon. The separation for zero potential between neon atoms is approximately $3\beta^{-1}$ (2.85 Å), that between argon atoms $2.15\beta^{-1}$ (3.45 Å). Consequently, we estimate this distance to be approximately $2.6\beta^{-1}$ for fluorine ions, by linear extrapolation on the basis of the β values for neon, fluorine, and argon. The weighting factor for the first shell of X ions in rutile is then zero, in fluorite positive (taken as 0.25), and in cristobalite negative (taken as −1). To investigate stability as a function of weighting factors, we choose also a value of zero at 2.15, and −1 at 2.62 and 3.04 (set $S2$); the set 0.25, 0, and −1, selected above on the basis of β values, is denoted by $S1$. In Table X the energy differences $\delta(C9\text{-}C4)$ and $\delta(C1\text{-}C4)$ between $C9$ and $C4$ and between $C1$ and $C4$ are given, first for pair interactions alone, and then for the two sets $S1$, $S2$ of weighting factors defined above. The three columns refer, respectively, to values $p=8$, 9, and 10 of the exponent p in the effective Born-Mayer pair repulsion. The symbol $C4$ stands for the structure $C4$-II; its parent configuration $C4$-I is excluded on the basis of higher pair repulsions (see Table IX). From the table we see, first of all, that *pair interactions* account correctly for the observed rutile stability of MgF_2, although stability with respect to $C9$ is low for $p=8$. Upon including three-ion interactions, the stability relations *shift markedly* with different choices of weighting factors for the first shell of X ions. For the most probable set ($S1$), the rutile stability is reproduced, both with respect to $C1$ and $C9$, whereby we observe that the rutile stability relative to $C9$ is *considerably higher than on the basis of pair interactions alone.*

On the other hand, displacing the first X shell towards the attractive part of the pair potential (set $S2$) results immediately in stability of the *fluorite* configuration; also the stability of rutile with respect to cristobalite is then greatly reduced. These results indicate *that the rutile lattice can be stable only in a narrow range of βR, γ values.* Upon increasing βR, the fluorite structure becomes more stable, primarily because the three-ion contribution from triplets $X_0X_1X_1$ is then quenched and stability is decided by triplets $A_0X_1X_1$ ($X_0A_1A_1$). On the other hand, if we decrease βR, retaining small values of $\gamma(<2)$, then the $C1$ structure is again more stable, as in the case of ZrO_2. Finally, upon increasing γ while decreasing βR, the stability shifts towards the cristobalite (quartz) configuration, as is illustrated in BeF_2 (see below).

A very different situation is encountered in the stability analysis of the compound TiO_2 ($\beta R=1.15$, $\gamma=4.2$), observed as a distorted rutile type and also as a distorted anatase structure. As for MgF_2, we first present the total pair repulsion, together with the *first-order* three-ion energies for triplets $A_0X_1X_1$ ($X_0A_1A_1$), $X_0X_1X_1$, and $X_0X_mX_m$ ($m\geqslant 2$). Since βR is here considerably smaller than for solid MgF_2, several more shells of X ions must be considered for stability; we have calculated the three-ion energies for $X_0X_mX_m$ triplets with $m=2, 3, \cdots, 10$. The results are given in Table XI, for TiO_2 in the structures $C1$, $C4$-I, $C4$-II, and $C9$. First we note that, as with MgF_2, three-ion interactions from triplets $A_0X_1X_1$ ($X_0A_1A_1$) are *attractive* in all configurations considered; they favor the fluorite structure. Three-ion energy from the first shell of X ions favors the rutile-I lattice; this gain in energy is, however, not preserved upon considering more distant shells. Qualitatively, it can already be seen that, al-

TABLE XI. Total pair repulsion $E_{\text{p.r.}}$ and first-order three-ion energies ΔE_1 for triplets $A_0X_1X_1$ $(X_0A_1A_1)$, $X_0X_1X_1$, and $X_0X_mX_m$, with $m=2, 3, \cdots, 10$, for TiO_2 in the structures C1, C4-I, C4-II, and C9. The quantity βR_m denotes the dimensionless distance from the mth shell to the central ion X_0. All energies are in units of nearest-neighbor repulsion.

TiO_2; $\beta R=1.146$, $\gamma=4.18$

Structure	$E_{\text{p.r.}}$	$A_0X_1X_1+X_0A_1A_1$	βR_1	$X_0X_1X_1$	βR_2	$X_0X_2X_2$	βR_3	$X_0X_3X_3$	βR_4	$X_0X_4X_4$	βR_5	$X_0X_5X_5$
C1	33.1229	−11.2058	1.32	−11.2079	1.87	−4.5089	2.29	−1.4540	2.65	−0.0688	2.96	−2.9366
C4-I	24.4328	− 5.5064	1.62	−13.0703	1.81	0.3320	1.98	0.2018	2.29	0.0689	2.43	−0.0427
C4-II	22.2468	− 5.0158	1.62	− 8.4122	1.98	0.1924	2.29	0.0287	2.56	−0.0440	2.77	−0.0103
C9	23.0521	− 1.7834	1.87	0.0989	3.24	−0.1660						

Structure	βR_6	$X_0X_6X_6$	βR_7	$X_0X_7X_7$	βR_8	$X_0X_8X_8$	βR_9	$X_0X_9X_9$	βR_{10}	$X_0X_{10}X_{10}$
C1	3.24	−0.8793								
C4-I	2.56	−2.0694	2.69	−0.0269	3.03	−0.0019	3.14	−0.0359	3.24	−0.5665
C4-II	2.81	−1.2776	2.99	−0.5681	3.21	−0.0272	3.24	0.0000		

though the packing of X shells in rutile I is very compact, the resulting three-ion energy does not favor the rutile structure by an appreciable margin.

To select the weighting factors for the X shells, we have to know the separation for zero pair potential between oxygen ions. Remembering that this distance, in units β^{-1}, is 3.0 for neon, 2.6 for fluorine ions, and 2.15 for argon, we choose a probable value of $2.4\beta^{-1}$ for the distance for zero pair potential between oxygen ions. Shells with βR_m values >2.4 are weighted by a factor -1 or -1.5, those for which $\beta R_m<2.4$ by a factor 0.5 or 0.5. In total, we selected the following sets of weighting factors:

$S1'$: 0.5 if $\beta R_m<2.4$; -1 if $\beta R_m>2.4$;

$S2'$: 0.5 if $\beta R_m<2$; 0.25 for $2<\beta R_m<2.4$ and -1 if $\beta R_m>2.4$;

$S3'$: 0.5 if $\beta R_m<2.4$; -1.5 if $\beta R_m>2.4$.

In Table XII we list the energy difference $\delta(C9\text{-}C4)$ between the β-cristobalite and rutile structures ($C4$ denotes $C4$-I; no significant difference exists between $C4$-I and $C4$-II), and the difference $\delta(C1\text{-}C4)$ between the fluorite and rutile structures, for the three above sets $S1'$, $S2'$, and $S3'$ of weighting factors for X shells. Also given are the values of these differences obtained on the basis of *pair interactions* only. The results are quite remarkable already on a two-body basis, since it is seen from the table that the rutile structure *is never stable:* for $p=9$ and 10, *fluorite* is the most stable structure, whereas for $p=8$, *cristobalite* is stable both with respect to rutile and to fluorite. Upon including three-ion forces, the fluorite structure *is always the stable one* for $p=8$, 9, and 10, *removing the ambiguity in stability with respect to p.* We have also found that the anatase structure is always less stable than rutile, both with pair interactions alone and including three-ion forces. The observed distortions of the real rutile or anatase lattice of TiO_2 cannot overcome such large differences in energy, since the Madelung constants of the distorted structures differ from those of the ideal lattices only by approximately 1%.[18] Apparently, the Ti^{4+} ion, although isoelectronic with argon, *cannot be considered only on the basis of closed-shell electron configurations.*

TABLE XII. Energy difference $\delta(C9\text{-}C4)$ between the cristobalite and rutile-I structures, and $\delta(C1\text{-}C4)$ between the fluorite and rutile-I structures (in kcal/mole), for TiO_2 as a function of weighting factors ($S1'$,$S2'$,$S3'$) for shells of X ions (defined in the text) and of the exponent $p=8$, 9, and 10 of the Born-Mayer effective pair potential.

	$\delta(C9\text{-}C4)$			$\delta(C1\text{-}C4)$		
TiO_2	$p=8$	$p=9$	$p=10$	$p=8$	$p=9$	$p=10$
pair interactions	−52.5	−21.2	3.8	−29.2	−45.6	−58.7
set $S1'$	−21.9	5.9	28.2	−71.2	−83.0	−92.4
set $S2'$	−21.8	6.1	28.4	−62.4	−75.1	−85.3
set $S3'$	−31.7	−27.5	20.4	−66.5	−78.8	−88.6

The last two compounds of this class to be discussed are SiO_2 ($\beta R=0.91$, $\gamma=15.4$) and BeF_2 ($\beta R=1.47$, $\gamma=12.3$), which exhibit $C8$, $C9$ stability. Only structures with 4,2-coordination must be compared for stability of these compounds, since those with higher coordination are ruled out on the basis of pair repulsions alone. In the following Table XIII we list, for SiO_2 in the structures β-cristobalite ($C9$), β-quartz ($C8$), and cuprite ($C3$), the same quantities as in Tables IX and XI. From the table we note that the pair repulsion is *lowest* in $C9$, somewhat larger in $C8$, and very much larger in $C3$. Triplets $A_0X_1X_1$ $(X_0A_1A_1)$ give, because of the same coordination, identical three-ion energies in the three structures. On the other hand, the first X shell in $C9$ develops much stronger repulsion than in $C8$; in $C3$ this three-ion energy is large and negative, because this shell in $C3$ has the same arrangement as the second shell of X ions in fluorite ($C1$). A *decisive* difference between $C8$ and $C9$ arises from three-ion interactions of triplets $X_0X_2X_2$; this second X shell is in the *repulsive* part of the pair potential for $C8$ ($\beta R_2=2.11$) and the resulting three-ion energy is *attractive,* whereas in the structure $C9$ this shell is already in the *attractive* part of the pair potential ($\beta R_2=2.58$), resulting in *repulsive* three-ion energy in this case. In addition,

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[18] K. Sahl, Acta Cryst. **19**, 1027 (1965).

TABLE XIII. Total pair repulsion $E_{\mathrm{p.r.}}$ and first-order three-ion energies ΔE_1 for triplets $A_0X_1X_1$ ($X_0A_1A_1$), $X_0X_1X_1$, and $X_0X_mX_m$, with $m=2, 3, \cdots, 8$, for SiO_2 in the structures β-cristobalite ($C9$), β-quartz ($C8$), and cuprite ($C3$). The quantity βR_m denotes the dimensionless distance from the mth shell of X ions to the central ion X_0. All energies are in units of nearest-neighbor repulsion.

SiO_2; $\beta R=0.912$, $\gamma=15.42$

Structure	$E_{\mathrm{p.r.}}$	$A_0X_1X_1+X_0A_1A_1$	βR_1	$X_0X_1X_1$	βR_2	$X_0X_2X_2$	βR_3	$X_0X_3X_3$	βR_4	$X_0X_4X_4$
$C9$	30.6028	−2.7942	1.49	3.9723	2.58	−4.6925	2.98	− 0.2866		
$C8$	35.2847	−2.7942	1.49	0.9776	2.11	−3.6825	2.29	− 0.7522	2.35	−1.6189
$C3$	62.8430	−2.7942	1.49	−31.4022	2.11	−1.8961	2.58	−25.4788	2.98	−0.2890

Structure	βR_5	$X_0X_5X_5$	βR_6	$X_0X_6X_6$	βR_7	$X_0X_7X_7$	βR_8	$X_0X_8X_8$
$C8$	2.73	−0.0641	2.79	0.0014	2.88	−0.5763	2.93	−0.0910

shells $m=3$ and 4 in $C8$ also develop attractive three-ion energy. Consequently, we see that the difference in three-ion interactions between $C8$ and $C9$ tends to compensate for the lower pair repulsion in $C9$. Using the same sets $S1'$, $S2'$, $S3'$ of weighting factors as defined in the analysis of TiO_2 stability, we obtain the results given in Table XIV for the differences in energy $\delta(C8\text{-}C9)$ between the β-quartz and β-cristobalite configurations, and $\delta(C3\text{-}C9)$ between the cuprite and β-cristobalite structures. First we observe that the cuprite structure is completely ruled out for stability, both for pair interactions and including three-ion forces. Further, the *cristobalite* configuration is considerably more stable than quartz on the basis of *pair interactions* alone (by about 3% of the total crystal energy). However, *upon including three-ion forces, their difference in stability disappears.* This result is qualitatively independent of the set of weighting factors chosen, i.e., stability of either structure is essentially determined by the symmetry properties of three-ion interactions and by the *sign* of the weighting factors for a few important shells of X ions. On the basis of the above results, we expect SiO_2 *to exhibit both C8 and C9 stability*, in striking agreement with experiment. Secondary effects, such as lattice distortions, will in each particular case decide stability of one, or another, of such configurations.

Finally, we consider crystal stability of BeF_2. In view of the relatively *large* value of βR compared to SiO_2 (1.47 compared to 0.91), pair energies are practically identical in $C8$ and $C9$. In addition, three-ion energies from triplets $A_0X_1X_1$ ($X_0A_1A_1$) as well as $X_0X_1X_1$ are the same in $C8$ and $C9$; further shells give no contribution to the crystal energy. The Madelung energy favors $C9$ over $C8$ by 11 kcal/mole; all energy differences are of this order of magnitude, i.e., only secondary effects, such as distortions, can stabilize either lattice.

TABLE XIV. Energy differences $\delta(C8\text{-}C9)$ between the β-quartz and β-cristobalite structures, and $\delta(C3\text{-}C9)$ between the cuprite and β-cristobalite structures (in kcal/mole), for SiO_2 as a function of weighting factors ($S1'$,$S2'$,$S3'$) for shells of X ions (defined in the text) and of the exponent values $p=8$, 9, and 10 of the Born-Mayer effective pair potential. Values of these differences on the basis of pair interactions alone are also given.

	$\delta(C8\text{-}C9)$			$\delta(C3\text{-}C9)$		
SiO_2	$p=8$	$p=9$	$p=10$	$p=8$	$p=9$	$p=10$
pair interactions	122.7	112.8	105	511	455	411
set $S1'$	−13.6	− 7.3	− 2.3	462	412	372
set $S2'$	6.4	10.5	13.7	469	418	377
set $S3'$	−36.1	−27.3	−20.3	561	500	451

Class (III). The AX_2 compounds which crystallize in the $C6$ or $C19$ structure are: ($C6$) $MgBr_2$, MgI_2; CaI_2; $SiTe_2$; TiS_2, $TiSe_2$, $TiTe_2$; ZrS_2, $ZrSe_2$, $ZrTe_2$; HfS_2, $HfSe_2$ and ($C19$) Cs_2O, $MgCl_2$. Further, we note from Table II that the βR values for compounds with the $C6$ configuration lie between 0.95 and 1.33, and that $C19$ stability occurs only in a narrow range of βR values, namely, between 1.4 and 1.5.

The comparison of static lattice energies of the nine different ideal structures, for compounds of this class, is carried out including polarization contributions, i.e., on the basis of Eq. (10) including E_{pol}. For the stable structure of each compound, Eq. (12) then applies, and E_{pol} can be determined as a function of the parameter p in the Born-Mayer effective pair repulsion, as we discussed in Sec. IV.

The principal task for the stability analysis of this class of compounds appears to be the explanation of the observed *relative stability* of the $C6$ (cadmium iodide) and $C19$ (cadmium chloride) configurations. In an earlier section we have already outlined this relative stability on a qualitative basis; we will now give the numerical results. Before doing this, we note that Ti compounds have also been included as members of this class ($C6$ stability), although from the analysis of TiO_2 stability we concluded that the Ti^{4+} ion cannot be considered only on the basis of closed-shell configurations. The justification is that we find the $C6$ structure for these compounds with large X ions to be considerably more stable than $C4$ (rutile), $C5$ (anatase), or any structure with 8,4 or 6,3 coordination. Consequently, such additional components of the crystal energy (stabilizing $C4$ for TiO_2) are unlikely to be of importance here.

For the analysis of $C6$, $C19$ relative stability we select $ZrSe_2$ ($\beta R=1.08$, $\gamma=4.8$) as an example. In Table XV we list for this compound the total pair repulsion $E_{\mathrm{p.r.}}$ and the *first-order* three-ion energies ΔE_1 for triplets $A_0X_1X_1$ ($X_0A_1A_1$) and $X_0X_nX_n$, with $n=1, 2, \cdots, 6$,

TABLE XV. Total pair repulsion $E_{\text{p.r.}}$, and first-order three-ion energies ΔE_1 for triplets $A_0X_1X_1$ ($X_0A_1A_1$) and $X_0X_nX_n$, with $n=1, 2, \cdots, 6$, for $ZrSe_2$ in the $C6$ and $C19$ configurations. The dimensionless distances βR_n, from the nth shell of X ions to the central ion X_0, are also given. All energies are in units of nearest-neighbor repulsion.

$ZrSe_2$; $\beta R=1.082$ $\gamma=4.81$

Structure	$E_{\text{p.r.}}$	$A_0X_1X_1+X_0A_1A_1$	βR_1	$X_0X_1X_1$	βR_2	$X_0X_2X_2$	βR_3	$X_0X_3X_3$	βR_4	$X_0X_4X_4$
$C19$	28.1227	−7.084	1.53	−11.2707	2.16	−0.6070	2.65	−8.3143	3.06	−0.0813
$C6$	28.1227	−7.084	1.53	−11.2494	2.16	−0.7662	2.50	0.0137	2.65	−5.5832

Structure	βR_5	$X_0X_5X_5$	βR_6	$X_0X_6X_6$
$C6$	2.93	−1.3777	3.06	−0.0178

together with the dimensionless distances βR_n from the nth shell of X ions to the central ion X_0. We conclude from the table that no appreciable differences between $C6$ and $C19$ arise from pair repulsions or from three-ion energies of triplets $A_0X_1X_1$ ($X_0A_1A_1$), $X_0X_1X_1$, and $X_0X_2X_2$. However, shells at $\beta R_n=2.65$, i.e., *the third X shell in C19 and the fourth X shell in C6, generate significantly different three-ion contributions to the crystal energy.* Since these shells are in the *attractive* part of the pair potential, their weighting factor $(1+E_{\text{attr}}^{(0)}/E_{\text{rep}}^{(0)})$ is negative, and the total (first- plus second-order) three-ion energy is repulsive, *more repulsive in C19 than in C6.* More distant shells have no appreciable effect on crystal stability. We conclude, therefore, that for these values of βR the *cadmium iodide* ($C6$) configuration is the more stable one, in agreement with experiment. When βR increases to about 1.4, then the above shells are at $\beta R_n \sim 3.6$ and their three-ion contribution has become negligible. For such large values of βR ($MgCl_2$, Cs_2O) the lattice energy of the ideal $C6$ and $C19$ structures is practically the same (except for a small difference in polarization energy of 1% in favor of $C6$). Distortion of the $C19$ lattice, resulting in an increase of the Madelung constant,[13] can then account for the observed $C19$ stability.

Finally, we give in Table XVI the complete results for the stability comparison between the nine ideal structures, selecting as typical examples $ZrSe_2$, MgI_2, and $MgCl_2$. The quantities listed are the same as those of Tables VII and VIII; in the last three columns δE denotes again the difference in energy between the structure considered and the stable one (in kcal/mole). The values in parentheses refer to the difference δE obtained on the basis of *pair interactions* only. We note from the table that a model of pair repulsions between the ions, extended to account for polarization contributions and for the different size of A and X ions (parameter γ), accounts correctly for observed stability relations. Of course, no distinction can be made on the basis of pair interactions between the stability of $C6$ and $C19$.

VI. SUMMARY AND DISCUSSION OF RESULTS

In this paper we have analyzed crystal stability of AX_2 compounds on the basis of pair interactions and of three-ion exchange forces in first and second orders of perturbation theory. The three-ion component of the interaction energy for each triplet of ions was calculated on the basis of effective, one-electron, charge distributions of Gaussian form for the ions, taking into account only single-exchange terms in the interaction energy. For a discussion of double exchange, and of the contribution from nonisosceles triangles of ion configurations we refer to [II]; the analysis given previously appears to apply equally well for AX_2 compounds. The *static* lattice energies of each compound in nine different (ideal) structures were compared for the *observed* value of the nearest-neighbor distance in the stable structure.

Further, polarization contributions to the crystal energy were taken to be of the form $-(\alpha/R^4)K$, where K is a characteristic lattice constant, R the nearest-neighbor distance, and where α is an effective polarizability of the X ion; values of α can be determined, in the framework of the Born-Mayer model, as a function of the exponent p in the Born-Mayer effective pair potential R^{-p}. The $C6$ (cadmium iodide) and $C19$ (cadmium chloride) lattices exhibit by far the largest value of K, so that polarization is of importance only in these layer structures. The calculation of K values for the nine different structures, as well as that of their Madelung constants, was carried out on the basis of the Bertaut method.

For all compounds considered, the stability results obtained upon including three-ion interactions were compared with those resulting from a pair-potential assumption only (however including polarization effects, which have appreciable Coulombic three-ion components). The pair potential is of the Born-Mayer type, extended to take into account the difference in size between A and X ions [through the parameter $\gamma=(\beta'/\beta)^2$, where β' and β are the Gaussian parameters for A and X ions]. This extended pair potential was found to yield stability results which are very close to the predictions based on the Goldschmidt rules, and which in some cases agree better with experiment. An example is ZrO_2: on the basis of ionic radii the predicted crystal structure is rutile,[7] whereas on the basis of γ-dependent pair repulsions we find fluorite as the stable lattice, in agreement with experiment.

The stability results for AX_2 compounds of which A

TABLE XVI. Madelung energy E_M (kcal/mole), total pair repulsion $E_{p.r.}$, three-ion energies from triplets $A_0X_1X_1$ ($X_0A_1A_1$) and $X_0X_nX_n$, summed over n, together with the sum of pair repulsions and total three-ion interactions (all in units of nearest-neighbor repulsion), for $ZrSe_2$, MgI_2, and $MgCl_2$ in nine different (ideal) configurations. In the last three columns the energy difference δE (kcal/mole) is given, for values $p=6$, 8, and 10 of the exponent p in the Born-Mayer effective pair repulsion. The numbers in parentheses refer to pair interactions only.

$ZrSe_2$; $\beta R=1.082$, $\gamma=4.81$

							δE	
Structure	E_M	$E_{p.r.}$	$A_0X_1X_1+X_0A_1A_1$	$\sum_n X_0X_nX_n$	$E_{p.r.}+\Delta E$	$p=6$	$p=8$	$p=10$
*C*1	−2509	40.0453	−5.7800	−2.8902	31.7351	802(960)	578(702)	444(548)
*C*4-I	−2382	29.7180	−2.8702	−3.2819	23.5659	664(781)	498(590)	398(475)
*C*4-II	−2370	27.1272	−2.6463	−2.0065	22.4744	641(717)	482(542)	387(437)
*C*5	−2316	28.1220	−3.2177	2.6086	27.5129	692(635)	531(485)	433(396)
*C*19	−2176	28.1227	−3.5420	2.6086	27.1893	0	0	0
*C*6	−2174	28.1227	−3.5420	1.1487	25.7294	45(0)	35(0)	29(0)
*C*9	−2218	9.2088	−0.9639	0.5294	8.7743	349(338)	287(278)	250(243)
*C*3	−2212	15.4285	−0.9639	−0.9979	13.4667	507(528)	412(429)	355(369)

MgI_2; $\beta R=1.227$, $\gamma=10.85$

							δE	
Structure	E_M	$E_{p.r.}$	$A_0X_1X_1+X_0A_1A_1$	$\sum_n X_0X_nX_n$	$E_{p.r.}+\Delta E$	$p=6$	$p=8$	$p=10$
*C*1	−571.4	72.1077	−7.9910	−10.7425	53.3742	205(339)	148(269)	115(227)
*C*4-I	−542.3	51.7958	−4.0735	−12.8355	34.8868	147(286)	110(236)	88(206)
*C*4-II	−539.8	45.9129	−4.0034	− 8.6304	33.2791	141(251)	106(207)	85(180)
*C*5	−527.6	47.8910	−3.9831	− 2.6371	41.2708	155(221)	118(182)	97(159)
*C*19	−495.4	47.9448	−3.9850	− 2.6371	41.3227	10(0)	8(0)	6.6(0)
*C*6	−495.0	47.9448	−3.9850	− 4.8454	39.1144	0	0	0
*C*9	−505.0	13.3798	−1.3262	− 0.0946	11.9590	73(143)	60(130)	53(122)
*C*3	−503.8	23.4539	−1.3262	− 2.7479	19.3798	110(189)	90(166)	77(152)

$MgCl_2$; $\beta R=1.417$, $\gamma=6.12$

							δE	
Structure	E_M	$E_{p.r.}$	$A_0X_1X_1+X_0A_1A_1$	$\sum_n X_0X_nX_n$	$E_{p.r.}+\Delta E$	$p=6$	$p=8$	$p=10$
*C*1	−658.7	38.1744	−6.8741	−2.0005	29.2998	296(290)	219(214)	172(169)
*C*4-I	−625.3	26.6846	−3.4500	−3.0724	20.1622	219(218)	166(165)	134(133)
*C*4-II	−622.2	22.9696	−3.3727	−2.5879	17.0090	184(187)	139(142)	112(114)
*C*5	−608.1	23.9297	−3.3142	−1.5424	18.0731	167(167)	128(128)	104(104)
*C*19	−571.1	23.9410	−3.3281	−2.5424	18.0705	0	0	0
*C*6	−570.6	23.9410	−3.3281	−2.4835	18.1294	0	0	0
*C*9	−582.2	7.3575	−0.9986	0.5910	6.9499	102(84)	83(70)	72(61)
*C*3	−580.7	10.7716	−0.9986	4.6108	14.3838	193(117)	155(96)	133(83)

is the larger ion, are very simple. We find fluorite (*C*1) stability with the Born-Mayer model, Goldschmidt rules, γ-dependent pair repulsions, and also upon including three-ion forces (Table VII). The three-ion energy for solids of these compounds, relative to the total pair repulsion, is of the order of 15% (attractive) for CaF_2, 5% (repulsive) for Na_2O, and 12% (attractive) for Li_2Se, all in the stable fluorite structure.

For AX_2 compounds with larger X ions we reproduce *C*1 stability for $SrCl_2$, ZrO_2, and HfO_2 on the basis of pair repulsions and also when three-ion interactions are included (Table VIII). In the latter case, the fluorite stability is approximately twice as large as with pair interactions alone. The three-ion energy in fluorite amounts, relative to the total pair repulsion, to 23% (attractive) for $SrCl_2$ and 35% (attractive) for ZrO_2 and HfO_2.

Of *particular importance* are the stability results for the compounds MgF_2 and TiO_2, observed in the *C*4 (rutile) type of lattice. These compounds have widely different βR values (1.86 and 1.15, respectively), whereas their γ values are small and of the same order. Between these two values of βR we observed *C*1 and *C*8, *C*9 stability (ZrO_2 and BeF_2). Pair interactions predict rutile as the stable structure for MgF_2, with a small stability margin with respect to cristobalite. Three-ion forces increase the stability of rutile relative to cristobalite; they show that the rutile configuration *can be stable only in a narrow range of* βR, γ *values* (Tables IX and X).

The situation is quite different for TiO_2 stability (Tables XI and XII). Although the Goldschmidt rules do predict rutile stability (ratio r_+/r_- between the radii of the ions is 0.55 for TiO_2 and 0.60 for MgF_2), we find that the smaller value of βR for TiO_2 causes further shells to contribute to the pair repulsion with a central ion. As a consequence, rutile stability is *ruled out* already on the basis of pair interactions; the stable structure is *fluorite* or *cristobalite*, depending upon the value of the parameter p in the effective Born-Mayer pair repulsion. When we include three-ion interactions, then *this ambiguity in stability is removed: fluorite* is the stable structure for TiO_2 for all values of p considered (8, 9, 10 and higher). Consequently, rutile stability of TiO_2 can be due only to an additional attractive component of the crystal energy which *cannot* be derived from pair-or three-ion interactions between closed shells of electrons. The origin of this stability must be related to the known different valency states of Ti, possibly involving Ti-Ti interactions *via* the oxygen ion.

For solids of the compounds SiO_2 and BeF_2 the βR values are again rather different (0.91 and 1.47), whereas the γ values are large and of the same order (15.4 and 12.3, respectively). In view of the large values of γ, only structures with 4,2-coordination have to be compared. If we consider, first, *pair interactions* only, then the cuprite ($C3$) configuration is excluded for stability because of large pair repulsion. Further, for BeF_2, there is no significant difference between the cristobalite ($C9$) and quartz ($C8$) structures. Upon including *three-ion* interactions, we find that for BeF_2 (large values of βR) this component is practically the same in the two structures. On the other hand, at *small* values of βR (SiO_2), pair repulsions in $C8$ are larger than in $C9$; also the Madelung energy favors cristobalite. Accordingly, on the basis of pair interactions, SiO_2 should be considerably more stable in the cristobalite than in the quartz configuration (by approximately 100 kcal/mole). *Three-ion interactions play a very important role* for stability of SiO_2: all triplets $X_0X_nX_n$ in $C9$ develop *repulsive* three-ion energy, whereas on the contrary, several shells in the quartz structure generate *attractive* three-ion interactions (Table XIII). As a result, the sum of non-Coulombic pair- and three-ion interactions favors the *quartz* configuration (Table XIV), compensating for the difference in Madelung energy between $C8$ and $C9$. Due to this important effect of three-ion interactions, we find that $C8$ and $C9$ are *very nearly of equal stability*, in agreement with experiment.

It has often been supposed that the stability of the quartz configuration arises from partial *covalent* bonding,[19] on the basis of the observation that the opening angle of the triplet O-Si-O in quartz is less than 180°, which is not favorable on a purely electrostatic basis. Indeed, the Madelung constant of $C8$ is 1% smaller than that of $C9$; also pair repulsion in $C8$ is larger than in $C9$. On the other hand, *strongly repulsive three-ion interactions*, involving triplets $X_0X_nX_n$ of *like* ions, are found in the $C9$ configuration, whereas these three-ion repulsions are completely *quenched* in $C8$ because of symmetry properties of three-ion interactions (Table XIII).

Finally, the relative stability of the $C6$ (cadmium iodide) and $C19$ (cadmium chloride) structures, for values of $\beta R<1.3$, was found to arise entirely from the difference in *three-ion* energy between these lattices. The shells of X ions which determine stability are the third shell in $C19$ and the fourth shell in $C6$, both at distance $6^{1/2}R$ from the central X ion. Corresponding triplets $X_0X_nX_n$ develop repulsive three-ion energy, more repulsive in $C19$ than in $C6$. This difference stabilizes $C6$ at small βR, since all other contributions to the crystal energy are very nearly the same. For βR values larger than about 1.4, the contribution from these shells to the three-ion energy is negligible. Accordingly, the crystal energy for the two structures is then practically the same, and the observed $C19$ stability for $MgCl_2$ and Cs_2O (βR between 1.4 and 1.5) must be due to secondary effects (distortion of the $C19$ lattice[13]).

A certain number of AX_2 compounds has been omitted from this stability analysis, because their crystal structures show too large deviations from an ideal lattice (e.g., $CaCl_2$, $BaCl_2$). Several intermediate configurations may be constructed by combining two sublattices of ions in the stoichiometric ratio 1:2; for some of these combinations electrostatic effects may often cause a lowering of the crystal energy with respect to an ideal structure. A typical example is the so-called $PbCl_2$ ($C22$) lattice, for which the coordination number is not well defined (between 6 and 8 for an A ion). The purpose of this paper was to investigate whether general stability relations for AX_2 compounds can be interpreted on the basis of pair- and three-ion interactions, taking as possible configurations nine ideal lattice types. An extension of this analysis to distorted and intermediate types of structures is not expected to introduce essentially different aspects of the stability problem for AX_2 compounds.

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