Calculation of Polarization Energies in Some III–VII and IV–VI Compounds with Stereochemically Active (ns)²-Ions

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The polarization energies of AB compounds, with A a monovalent or divalent cation with an (ns)²-lone pair and B an anion with a noble gas electronic configuration, have been calculated to investigate whether the stereochemical activity of the (ns)²-ion can be understood in an ionic picture. Computations have been performed applying the computer program EWALD. Formal ionic charges and partly estimated polarizabilities have been used. The polarization energy is shown to be predominantly due to cation polarization and may constitute an appreciable fraction of the total lattice energy. Hence, it can play a crucial role in the formation of structures, in which the (ns)²-ion is in a noncentrosymmetrical environment.

1. Introduction

Ions with an (ns)² outer electronic configuration are often stereochemically active (1–4). Residing in an originally centrosymmetrical environment, they tend to distort this to become noncentrosymmetrical. Examples of distorted structures are, e.g., β-TlI (5), α- and β-InCl (6), and β-TlF (7). Further examples are presented in Section 3.

Under the influence of the "ungerade" deformations the spherical s orbital, in which the "lone pair" is situated, is mixed with an excited p orbital, giving an aspherical hybrid. There exist several driving forces for this type of lattice distortion with accompanying electron redistribution. Two covalent sources of deformation, both favoring s–p mixing, are the repulsion between the electron pairs, lone pair, and bonding pairs, in the valency shell of the (ns)²-particle (8–10), and the strengthening of covalent bonds by a larger overlap (11).

We intend to study the stereochemical activity from an ionic point of view, in which the most important driving force is due to electric polarization (1). Owing to an "ungerade" deformation an ion experiences a non-zero electric field **E**, which induces an electronic dipole moment $\mu = \alpha\mathbf{E}$ (α is the dipolar polarizability). The energy of this dipole in the electric field is $-\mu \cdot \mathbf{E} = -\alpha E^2$. The distortion is

counteracted by mainly two energy terms. First, the hybridization energy, which is in the ionic picture approximately $\mu^2/2\alpha = \frac{1}{2}\alpha E^2$, so that the net polarization energy is $-\frac{1}{2}\alpha E^2$. Second, the elastic energy of the crystal, mainly consisting of the change of the madelung energy caused by the deformation. Whether distortion will take place or not depends on the interplay of all energy terms. The stereochemical activity of (ns)^2-ions can be explained by the small energy separation between the (ns)^2-^{1}S ground and (ns)(np)-^{1}P excited states, leading to a small hybridization energy or a large polarizability. (ns)^2-ions have a larger polarizability than ions of the same radius with a noble gas configuration (1).

Theoretical calculations have been performed mainly on free AB_6-octahedra (A = (ns)^2 − cation; B = anion) ($1, 12$), like, e.g., XeF$_6$ molecules (13–15). Most of the calculations on free octahedra were based on crystal field theory. Only a few energy calculations on crystals with (ns)^2-ions have been performed, e.g., on β-TlF (7). Surprisingly, in this calculation the polarization energy terms were omitted completely.

Here we shall present the first energy calculations on AB compounds with A an (ns)^2-cation, in which polarization energies have been taken into account. In order to investigate how the existence of distorted AB compounds can be understood in an ionic picture it will be shown that:

(1) the polarization energy certainly should not be neglected in energy calculations, as it is an appreciable energy term, which might lead to an energy balance favoring the distorted structure;

(2) the polarization energy is rather due to the cation than to the anion polarization.

To this purpose the polarization energies of a number of distorted AB compounds have been calculated in a semiquantitative way.

The bonding is assumed to be purely ionic, which undoubtedly applies more to III–VII than to IV–VI compounds.

For the calculation of potentials and fields in the lattice and of the madelung and the polarization energy the computer program EWALD was used ($16, 17$). This program is based on the Ewald method in which the various lattice sums, originally to be performed in real space, are split up into two faster converging parts. One summation is still performed in real, the other in reciprocal space. The potentials and fields due to the monopoles and induced dipoles are calculated, whereas higher order multipoles are neglected. The electric fields are solved in a self-consistent way. For a further explanation of the program we refer to the above references. The assumptions and approximations of the calculations are summarized in Section 2.1; in Section 2.2 the choice of the polarizability values α is discussed. The results are presented in Section 3 and the discussion in Section 4.

2. The Calculational Procedure

2.1. The Model

In the ionic picture a crystal of ions is represented by a lattice of point charges (monopoles) and coinciding induced higher order multipoles. Overlap between the charge clouds is neglected. If, in addition, the quadrupole moments and still higher order moments are neglected, a system of monopoles q_i and induced dipoles μ_i at ion sites i remains. The potential V_i at site i is a sum of contribution V_i^m, due to all monopoles at other sites, and V_i^d, due to all induced dipoles at other sites: $V_i = V_i^m + V_i^d$. In the purely ionic picture q_i is taken equal to the formal charge q_i^f. The induced dipole μ_i is assumed to be proportional to the total electric field $\mathbf{E}_i$ at site i: $\mu_i = \vec{\alpha}_i \cdot \mathbf{E}_i$, in which $\vec{\alpha}_i$ is the dipolar polarizability. In principle $\vec{\alpha}_i$ is a tensor, but here it will be approximated by a scalar quantity.

With the above approximations the total field $\mathbf{E}_i$ at site i is the sum of a "monopole field" $\mathbf{E}_i^m$, due to all monopoles at other sites, and a "dipole field" $\mathbf{E}_i^d$, due to all induced dipoles at other sites: $\mathbf{E}_i = \mathbf{E}_i^m + \mathbf{E}_i^d$. As $\mathbf{E}_i^d$ depends on the induced dipoles and vice versa, $\mathbf{E}_i$ has to be solved self-consistently for all different ion sites.

The total energy is the sum of madelung and polarization energy:

$$E = E_{mad} + E_{pol}.$$

The term E_{pol} now can be regarded as the sum of a "monopole" part E_{pol}^m, i.e., the polarization energy with neglect of dipole fields, and a "dipole" part E_{pol}^d, the "extra" polarization energy resulting from the inclusion of dipolar fields:

$$E_{pol} = E_{pol}^m + E_{pol}^d.$$

By definition:

$$E_{mad} = \tfrac{1}{2}\Sigma_i q_i V_i^m,$$

where the summation runs over all ions, and

$$E_{pol}^m = -\tfrac{1}{2}\Sigma_i \alpha_i \mathbf{E}_i^m \cdot \mathbf{E}_i^m$$

$$E_{pol}^d = -\tfrac{1}{2}\Sigma_i \alpha_i \mathbf{E}_i^m \cdot \mathbf{E}_i^d$$

$$E_{pol} = -\tfrac{1}{2}\Sigma_i \alpha_i \mathbf{E}_i^m \cdot \mathbf{E}_i.$$

Hence

$$E = \tfrac{1}{2}\Sigma_i (q_i V_i^m - \alpha_i \mathbf{E}_i^m \cdot \mathbf{E}_i).$$

E also can be expressed as

$$E = \tfrac{1}{2}\Sigma_i q_i V_i.$$

It should be remarked that the equation

$$\Sigma_i q_i V_i = \Sigma_i (q_i V_i^m - \alpha_i \mathbf{E}_i^m \cdot \mathbf{E}_i),$$

holding for the summation over all ions, holds for neither the individual terms of the summation nor the summations over the anions or the cations only. The polarization energy can be written as the sum of the cation part:

$$E_{pol}(cat) = -\tfrac{1}{2}\Sigma_c \alpha_c \mathbf{E}_c^m \cdot \mathbf{E}_c,$$

and the anion part:

$$E_{pol}(an) = -\tfrac{1}{2}\Sigma_a \alpha_a \mathbf{E}_a^m \cdot \mathbf{E}_a,$$

in which the summations run over the cations $i = c$ and anions $i = a$.

The main assumptions of the model will be summarized now: (a) the multipole expansion of charge clouds and the neglect of overlap; (b) the truncation of the multipole expansion after the dipolar terms; (c) the use of charges equal to the formal charges; (d) the relation $\mu = \alpha E$, with α a scalar quantity; and (e) the choice of α. In particular the neglect of overlap, and hence the occurrence of covalent bonding and the nonequality of real and formal charges due to this bonding, can give rise to serious errors. Fortunately, the effects of these approximations are opposite: covalent bonding will give an energy decrease. On the other hand it leads to charges $q = fq^f$, which in absolute value are smaller than the formal charges (ionicity $f < 1$). Hence, the ionic contribution to the energy becomes less negative resulting in an energy increase.

The dependencies of the calculated energy terms on q are:

$$E_{mad} \sim q; \quad E_{pol}^m, E_{pol}^d, E_{pol} \sim q^2,$$

so, a deviation of f from unity especially affects those polarization energy terms, which are quadratic in q. Furthermore, the deviation of f from 1 may be expected to increase with increasing q^f, as the bonds become more covalent. Probably, covalency ($f < 1$) will lead to only small errors in the calculations of the energies of the III–VII compounds and to considerable errors for the IV–VI compounds.

Another important source of error is the value of the polarizabilities. In the next section it will be shown that polarizabilities are difficult to obtain. Hence, any value used in the present calculations must be regarded as a rough approximation. In the AB compounds with $\alpha(cat)$ the cation and

α(an) the anion polarizability, the following dependencies on the polarizabilities exist:

V_i^m, E_i^m: none

V_i^d, E_i^d: linear in α(cat) and α(an), and higher order terms including mixed terms

E_{mad}: none

E_{pol}^m(cat): linear in α(cat); E_{pol}^m(an): linear in α(an)

E_{pol}^d(cat): quadratic term in α(cat), mixed α(cat) α(an) bilinear term and higher order terms

E_{pol}^d(an): quadratic term in α(an), mixed α(cat) α(an) bilinear term and higher order terms.

While an error in the polarizabilities affects the monopole term of the polarization energy in a linear way, that in the dipole terms is more serious. It will depend on the relative magnitudes of E_{pol}^m and E_{pol}^d, how reliable the value of the calculated total E_{pol} will be.

2.2 Polarizability

The apparent polarizability α of an ion, which is needed as an input parameter in the present calculations, has been defined as the proportionality factor between the induced electronic dipole moment of this ion and the total internal electric field at the experimentally determined ion position (Section 2.1; refs. 16, 17). However, experimentally determined polarizabilities depend on both the frequency of the electric field-strength fluctuation and the spatial coordination of the ions (cf. ref. 18). Moreover, they are determined at much lower field-strengths than exist in chemical compounds (19). Therefore, it is not self-evident which experimental value would be the most appropriate one. On the other hand, the available data hardly offer a choice. We have taken structure-averaged

optical polarizabilities from Tessman et al. (20), α_{opt}^{TKS}, as far as these are known (Table I; 20, 21). For (ns)²-ions it can be shown that α_{opt}^{TKS} is suitable as an approximation for the apparent polarizability (22). For lack of better values α_{opt}^{TKS} was also used for the noble gas configuration anions. For the chalcogenide ions the mean values in Table I were taken.

The polarizabilities of In⁺, Sn²⁺, and Ge²⁺ are unknown, but we have used an estimation (Table II) based on the approximate charge-invariance of the polarizability in a series of isoelectronic (ns)² particles, as was noticed by Jørgenson (23, 24) in the series of (6s)² particles Hg, Tl⁺, Pb²⁺ ($\alpha \approx 5$ for $n = 6$: cf. Table I). If an analogous invariance for $n = 5$ and $n = 4$ is assumed, also charge-independent approximate α-values can be found for the (5s)² series Cd, In⁺, Sn²⁺, and the (4s)² series Zn, Ga⁺, Ge²⁺, as the polarizabilities of Cd and Zn are known (21) (Table II). The maximum of α at $n = 5$ is probably due to a minimum of the energy of the excited (ns)(np)-¹P excited state in the chemical compounds (22), analogous to the experimentally found minimum for the gaseous ions (25).

TABLE I

POLARIZABILITY α_{opt}

Polarizability α_{opt} of some ions and atoms with an (ns)²-configuration[a]

$n =$			
4	Zn: 6(21)	Ga⁺: —	Ge²⁺: —
5	Cd: 8(21)	In⁺: —	Sn²⁺: —
6	Hg: 5.1(21)	Tl⁺: 5.2(20)	Pb²⁺: 4.9(20)

Polarizability α_{opt} of some ions with a noble gas configuration (ns)²(np)⁶[b]

$n =$		
2	·F⁻: 0.64	O²⁻: 0.5– 3.2 (mean: 1.9)
3	Cl⁻: 2.96	S²⁻: 4.8– 5.9 (mean: 5.4)
4	Br⁻: 4.16	Se²⁻: 6.0– 7.5 (mean: 6.8)
5	I⁻: 6.43	Te²⁻: 8.3–10.2 (mean: 9.25)

[a] In Å³; references are in parentheses.
[b] From ref. (20).

TABLE II

Estimated Polarizabilities
for Isoelectronic $(ns)^2$
Particles

n	α
4	6
5	8
6	5

3. Results

The present paper deals with the III–VII compounds: α- and β-InCl (6); InBr, InI, and β-TlI (5); β-TlF (7) and the IV–VI compounds: α-GeTe (26); GeSe, GeS, SnS, and SnSe (27); α-PbO, and β-PbO (5). The structural information can be found in the above references. In this paper axes are chosen according to the convention of the International Tables (28). A change of the coordinate system of the original authors is straightforward.[1] The structure of α-InCl is a complicated distortion of the rocksalt or B1 structure (6, 29). β-InCl, InBr, InI, and β-TlI have the so-called B33 structure, which can be derived from the B1 structure (30, 29), but also from B2 (30). GeSe, GeS, SnS, and SnSe have the B29 structure, which has much in common with the B33 structure. The β-TlF and β-PbO structures are very much alike and are also distorted B1 structures. In fact, the derivation of β-TlF, β-PbO, B33, and B29 from the B1

[1] Conversion of coordinate systems was as follows ("or" means original):

β-TlF(7): $Pm1a \rightarrow Pma2$; $a = a^{or}$; $b = c^{or}$; $c = b^{or}$.

α-GeTe(26): In the original paper the almost cubic chemical cell of the B1 structure, with $Z = 4$, was used ($a^{or} = 5.996$ Å; $\alpha^{or} = 88.18°$). We use the primitive cell with $Z = 1$ (space group $R3m$; $a = a^{or} \cos(\frac{1}{2}\alpha^{or}) = 4.307$ Å; $\alpha = 2$ arc sin ($\frac{1}{2}tg(\frac{1}{2}\alpha^{or})$) = 57.94°).

SnS, SnSe, GeS, GeSe(27): $Pbnm \rightarrow Pnma$; $a = b^{or}$; $b = c^{or}$; $c = a^{or}$.

α-PbO(3): Origin was shifted from position $\bar{4}m2$ to $2/m$ in $P4/nmm$.

β-PbO(3): $Pbma \rightarrow Pbcm$: $+ = c^{or}$; $b = a^{or}$; $c = b^{or}$.

structure can go through one common intermediate step, the hypothetic "B1a" structure (22, 29, 31). α-GeTe is a deformation of B1 and is isomorphous with grey As, Sb, and Bi, if A and B are regarded as the same particle in this AB compound (26). Similarly, the B29 structure type resembles that of black phosphorus (27). The structure of α-PbO (5) can be regarded as a distortion of CsCl or B2.

The potentials and electric fields at the ion sites, which have been calculated with the EWALD program, are given in Tables III (III–VII compounds) and IV (IV–VI compounds). From these the madelung energy and the polarization energy terms E_{pol}^m and E_{pol}^d, together with their sum E_{pol}, can be calculated using the formulas of Section 2.1. The result is given in Table V. The contributions to the polarization energies from the anions and the cations are given in Table VI.

Table III shows that inclusion of dipole fields has important consequences. The electric field strength has changed appreciably. For the cations the changes are both positive and negative. The changes for the anions always are positive and large: in most cases E is even an order of magnitude larger than E^m. That the change is larger for the anions can be explained by the large dipole moments of the cations, which are already large in the monopole approximation. Note that also the direction of the field is influenced by the dipolar fields. Again the change is largest for the anions: in most cases the field direction is even reversed. This is unfavorable for the polarization energy, as can be expected from the formula of E_{pol}(an) (Section 2.1): a reversed direction gives a positive energy contribution. Indeed E_{pol}(an) is positive, though small, in the III–VII compounds (Table VI), while E_{pol}(cat) is negative and larger in magnitude. This is because both E^m and E are large for the cations and their scalar product is positive (Table III). The total

TABLE III

CALCULATED POTENTIALS AND FIELDS: III–VII COMPOUNDS[a]

Compound	Ion	V^m	E^m	E_x^{m*}	E_y^{m*}	E_z^{m*}	V	E	E_x^*	E_y^*	E_z^*
α-InCl	In(1)	−7.424	1.524	−0.046	0.782	1	−7.961	1.674	0.105	0.746	1
	In(2)	−7.554	2.295	1	−0.587	−0.667	−8.437	1.794	1	−0.468	−0.641
	In(3)	−7.790	1.700	−1	−1	−1	−8.032	2.278	−1	−1	−1
	In(4)	−7.542	2.382	1	1	1	−8.642	1.841	1	1	1
	Cl(1)	7.416	0.278	1	−0.540	−0.342	8.377	1.373	−1	0.895	0.078
	Cl(2)	7.492	0.469	−0.138	−0.482	−1	9.032	1.769	−1	−0.829	0.980
	Cl(3)	7.759	0.292	1	1	1	8.861	1.326	1	1	1
	Cl(4)	7.491	0.453	1	1	1	8.482	1.895	−1	−1	−1
β-InCl	In	−7.603	1.740	0	−1	0	−8.190	2.061	0	−1	0
	Cl	7.504	0.527	0	1	0	8.637	2.528	0	−1	0
InBr	In	−7.498	1.861	0	−1	0	−8.880	3.956	0	−1	0
	Br	7.334	0.327	0	1	0	9.560	5.110	0	−1	0
InI	In	−6.834	1.393	0	−1	0	−7.485	2.147	0	−1	0
	I	7.036	0.487	0	1	0	7.678	1.699	0	−1	0
β-TlI	Tl	−6.961	0.817	0	−1	0	−7.091	1.001	0	−1	0
	I	7.085	0.244	0	1	0	7.203	0.441	0	−1	0
β-TlF	Tl(1)	−8.538	3.272	0	0.341	−1	−8.585	1.761	0	0.675	−1
	Tl(2)	−9.788	3.720	0	0.136	1	−10.083	3.092	0	0.255	1
	F(1)	7.726	1.709	0	0.225	1	9.586	2.048	0	0.768	−1
	F(2)	7.687	1.117	0	−0.270	−1	11.392	2.624	0	0.070	1

[a] See footnote a to Table IV.

TABLE IV

CALCULATED POTENTIALS AND FIELDS: IV–VI COMPOUNDS[a]

Compound	Ion	V^m	E^m	E_x^{m*}	E_y^{m*}	E_z^{m*}	V	E	E_x^*	E_y^*	E_z^*
α-GeTe	Ge	−16.872	0.679	−1	−1	−1	−15.925	4.420	1	1	1
	Te	16.872	0.679	−1	−1	−1	16.247	4.343	1	1	1
GeSe	Ge	−17.297	3.924	1	0	0.623	−32.647	27.132	0.624	0	1
	Se	17.110	1.260	0.208	0	−1	31.483	33.271	0.355	0	−1
GeS	Ge	−18.115	4.572	1	0	0.657	−27.823	17.016	0.589	0	1
	S	17.782	1.567	0.096	0	−1	28.778	21.567	0.342	0	−1
SnS	Sn	−17.006	3.724	1	0	0.507	−23.946	17.069	0.461	0	1
	S	16.750	0.906	−0.295	0	−1	26.589	21.246	0.347	0	−1
SnSe	Sn	−16.321	3.224	1	0	0	−29.226	31.840	0.489	0	1
	Se	16.205	0.684	−0.152	0	−1	31.343	39.008	0.360	0	1
α-PbO	Pb	−20.492	7.497	0	0	−1	−20.212	5.526	0	0	−1
	O	16.912	0.000	0	0	0	24.241	0.000	0	0	0
β-PbO	Pb	−20.584	7.693	−1	−0.322	0	−20.552	14.602	0.013	−1	0
	O	17.107	2.198	1	−0.339	0	25.017	21.745	0.512	−1	0

[a] "Ion" is the ion on which the potential (V) and electric field ($\mathbf{E}$) is calculated. E_α^* is the relative component of $\mathbf{E}$ along the α-axis ($\alpha = x, y, z$), normalized to the largest value. Results of monopole calculations excluding dipolar fields are labeled with the superscript m. V is in volts; E in volts/Å. Convergence of lattice sums was reached within 0.001%.

polarization energy E_{pol} (Table V) is always negative for the III–VII compounds and is of the order of some 10% of the madelung energy, which is appreciable. The influence of the dipole fields on the polarization energy cannot be neglected but is not extreme for the III–VII compounds (Table V).

For the IV–VI compounds inclusion of dipole fields has enormous effects. All field strengths become much larger (Table IV). The change is largest for the anions amounting to even an order of magnitude. The scalar product of $\mathbf{E}^m$ and $\mathbf{E}$ is positive, for both cations and anions. The only exception is α-GeTe, in which the field direction is reversed on both ions. Therefore, E_{pol}(cat) and E_{pol}(an) (Table VI) and hence their sum E_{pol} (Table V) are negative, except for α-GeTe.[2] The polarization energy is very large and is also influenced very much by the dipole fields. E_{pol} is of the order of half E_{mad} for the B33 compounds and about one-fifth of E_{mad} for both modifications of PbO.

4. Discussion

The question posed in this paper was to show, in an ionic picture, whether the po-

[2] The method in which the linear equations $\mu_i = \alpha_i \mathbf{E}_i$ are solved self-consistently is equivalent to the more fundamental method in which the total energy, consisting of monopole–monopole, monopole–dipole, dipole–dipole interaction and a harmonic self-energy term $\mu_i^2/2\alpha_i$ per ion, is minimized with respect to the variables μ_i, provided that such a minimum exists. This implies that the quadratic part of the energy, consisting of self-energies and bilinear dipole–dipole terms, must be positive definite. For too large values of α_i this requirement is not satisfied and the system described with only harmonic self-energies is unstable with all μ_i running to infinity. The extremum of such a system, which is also found when solving the self-consistency equations, is then not a minimum but some saddle point in μ-space. This situation is met in α-GeTe, as a positive value of E_{pol} cannot correspond to an energy minimum. In order to stabilize the system fourth order self-energy terms should be taken into account, leading to a breakdown of the linear relation between μ_i and $\mathbf{E}_i$.

TABLE V

ENERGIES[a]

Compound	E_{mad}	E_{pol}^m	E_{pol}^d	E_{pol}
α-InCl	−173.19	−25.42	+3.52	−21.90
β-InCl	−174.08	−20.05	+0.24	−19.81
InBr	−170.91	−22.53	−19.04	−41.57
InI	−159.83	−13.65	−1.24	−14.89
β-TlI	−161.85	−3.09	+0.24	−2.85
β-TlF	−194.38	−52.14	+18.11	−34.03
α-GeTe	−777.62	−5.62	+41.84	+36.22
GeSe	−792.90	−82.57	−602.40	−684.97
GeS	−827.24	−110.95	−366.17	−477.13
SnS	−777.90	−92.32	−294.37	−386.69
SnSe	−749.56	−69.06	−578.11	−647.17
α-PbO	−861.98	−220.39	+57.96	−162.43
β-PbO	−868.60	−239.41	+57.87	−181.55

[a] kcal/mole.

larization energy due to the distortion of a high symmetry AB structure, as B1, can be large enough to overcompensate any energy increase brought about by such distortions, resulting in a total energy, that favors the distorted structure. To answer this question it would be necessary to calculate both the polarization and the deformation energy as a function of the distortion and to minimize the total energy with respect to the deformation parameter(s). This is problematic, however, as (1) the prototype phase is unknown for most compounds, since it does not exist as a high temperature modification, and (2) the calculations would involve accurate calculations of, among other contributions, exchange repulsion.

It should be noted that, even if this procedure were possible, and the answer to the question posed affirmative, it does not mean that the bonding in the studied compound is predominantly ionic. In general, the energy is not very sensitive to the nature of the bonding (32).

To get a first indication of the effects, the polarization energy term together with the madelung energy is calculated semiquantitatively in the crystal structures found in nature. The polarization energy, calculated for an ionic model with formal charges and

TABLE VI

CATION AND ANION CONTRIBUTION TO THE POLARIZATION ENERGY[a]

Compound	E_{pol}^m(cat)	E_{pol}^m(an)	E_{pol}^d(cat)	E_{pol}^d(an)	E_{pol}(cat)	E_{pol}(an)
α-InCl	−25.08	−0.35	+2.55	+0.98	−22.53	+0.64
β-InCl	−19.38	−0.66	−3.58	+3.82	−22.96	+3.16
InBr	−22.15	−1.42	−24.95	+6.98	−47.10	+5.56
InI	−12.42	−1.22	−6.73	+5.48	−19.15	+4.26
β-TlI	−2.78	−0.31	−0.62	+0.87	−3.40	+0.56
β-TlF	−51.06	−1.07	+15.72	+2.38	−35.34	+1.31
α-GeTe	−2.21	−3.41	+16.61	+25.23	+14.40	+21.82
GeSe	−73.93	−8.64	−385.07	−217.33	−459.00	−225.97
GeS	−100.35	−10.61	−234.79	−131.38	−335.14	−141.99
SnS	−88.78	−3.54	−230.27	−64.10	−319.05	−67.64
SnSe	−66.52	−2.54	−452.99	−125.12	−519.51	−127.66
α-PbO	−220.37	0	+57.94	0	−162.43	0
β-PbO	−232.06	−7.35	+102.63	−44.77	−129.43	−52.12

[a] The cation and anion contributions to the polarization energy terms E_{pol}^m and E_{pol}^d and their sum, E_{pol}, are the summations, mentioned in Section 2.1, in which i runs only over the cations respective to the anions.

partly estimated polarizabilities, varies always between appreciable and large (Section 3). Furthermore it is shown (Table VI) that this polarization energy is for the larger part due to polarization of $(ns)^2$-cations.

As to the reliability of the calculated energies it was remarked in Section 2.1 that covalency effects ($f < 1$) will most affect the results of the IV–VI compounds, in particular the polarization energy terms. The inaccuracy in α leads also to errors in the polarization energies, especially in the dipole term. As the latter is very large for the IV–VI compounds (Table V and VI), the calculated E_{pol} of IV–VI compounds cannot be expected to be reliable: only the

TABLE VII

COMPARISON OF ENERGY WITH IDEALIZED B1 STRUCTURE[a]

Compound	a_0	E_{mad}^{id}	ΔE_{mad}	ΔE	ΔE_{mad}^{corr}	E_{pol}^{corr}	ΔE^{corr}
α-InCl	6.1865	−187.46	+14.27	−7.63	+12.84	−14.20	−1.36
β-InCl	6.2634	−185.16	+11.08	−8.73	+9.97	−11.96	−1.99
InBr	6.3972	−181.29	+10.38	−31.19	+9.34	−19.23	−9.89
InI	6.6804	−173.60	+13.77	−1.12	+12.39	−8.56	+3.83
β-TlI	6.7887	−170.83	+8.98	+6.13	+8.08	−1.78	+6.30
β-TlF	5.5915	−207.41	+13.03	−21.00	+11.73	−25.85	−14.12
α-GeTe	5.9945	−773.86	−3.76	+32.46	−3.38	+9.18	+5.80
GeSe	5.6796	−816.76	+23.86	−661.11	+21.47	−230.26	−208.79
GeS	5.4921	−844.65	+17.41	−459.72	+15.67	−176.42	−160.75
SnS	5.7892	−801.30	+23.40	−363.29	+21.06	−143.70	−122.64
SnSe	5.9700	−777.03	+27.47	−619.70	+24.72	−214.87	−190.15
β-PbO	5.3850	−861.45	−7.15	−188.70	−6.44	−126.29	−132.73

[a] The energies of Table VI are compared with those of undistorted B1 structures with cell axis a_0(Å), and madelung energy E_{mad}^{id}. The difference in madelung energy is $\Delta E_{mad} = E_{mad} - E_{mad}^{id}$, $\Delta E = \Delta E_{mad} + E_{pol}$. The superscript corr means that a correction for the exchange interaction is applied. This table shows the competition between the energy decrease E_{pol}^{corr} and the energy increase ΔE_{mad}^{corr} due to distortion. All energies are in kcal/mole.

order of magnitude may be correct. For the III–VII compounds, on the other hand, E_{pol}^d is always smaller than E_{pol}^m. Because of this and because of the expected smaller covalency, the calculated E_{pol} may be a nice approximation.

In these calculations the exchange repulsion between the ions has not been included so far. The effect of this exchange repulsion on the preceding results may be roughly described. Suppose the exchange energy of a crystal is represented by a Huggins–Mayer type expression (33)

$$B \exp \left[\frac{-(r - r_0)}{\rho} \right],$$

in which r is some linear variable of the system, e.g., a cell axis, and r_0 its equilibrium value; B and ρ are parameters. Usually ρ/r_0 is approximately 0.1 (34). The madelung and polarization energy terms can be written as:

$$E_{mad} = A_1/r$$

$$E_{pol}^m = A_4/r^4$$

$$E_{pol}^d = A_7/r^7 + \text{(higher order terms in } r^{-1} \text{ which will be neglected).}$$

If the total energy is written as the sum of the above terms, plus exchange energy, and is minimized with respect to r, then in the minimum:

$$E(r = r_0) = (1 - \rho/r_0)A_1/r_0$$
$$+ (1 - 4\rho/r_0)A_4/r_0^4 + (1 - 7\rho/r_0)A_7/r_0^7.$$

This means that the madelung energy is compensated for some 10% by exchange repulsion, the monopolar polarization energy for some 40%, and the dipolar polarization energy for even 70%. Therefore, the corrected values of these energy terms are some 90, 60, and only 30%, respectively, of the original values. Hence large errors in E_{pol}^d are suppressed appreciably.

It would be interesting to show that the cations in the compounds studied are at a position of minimal energy by slightly varying the cations coordinates and calculating the energy. However, such a calculation would need a very refined expression for the exchange repulsion between two ions, which is dependent upon the polarization state of the ions. Unfortunately such an expression is not available.

For the same reason a minimization procedure of the total energy, as a function of some distortion parameters, which are zero in the undistorted phase, would be impossible, moreover, as this prototype phase does not occur in nature, as an alternative modification of the compound (except α-TlI with the B2 structure).

All compounds studied, except α-PbO, can be considered as distorted B1 structures (31), while the B33 structure can also be derived from B2 (30). It would be interesting to compare the calculated energies with the madelung energy of a hypothetical B1 structure, with cell axis a_0. Assuming the totally symmetrical strain component in a hypothetical phase transition between this B1 modification and the actual structure equal to zero, the value of a_0 can be calculated according to ref. (31) (Table VII). The madelung energy of the B1 phase, E_{mad}^{id}, and the energy comparison is given in Table VII. It is found that $\Delta E_{mad} = E_{mad} - E_{mad}^{id}$, which is the largest part of the distortion energy, is positive, except for α-GeTe and β-PbO, and that $\Delta E = \Delta E_{mad} + E_{pol}$ is negative, except for β-TlI and α-GeTe. If the values of E_{mad}, E_{pol}^m, and E_{pol}^d are corrected for Born repulsion, in the above approximation with $\rho/r_0 = 0.1$, then the corrected values ΔE_{mad}^{corr}, E_{pol}^{corr}, and ΔE^{corr} can be obtained (Table VII). For all compounds ΔE^{corr} is negative, with the exception of InI, β-TlI, and α-GeTe, for which it amounts to some $+5$ kcal/mole.

It is shown in the present paper that predominantly due to cation polarization

the distortion leads to a substantial polarization energy, which is either of the same order of magnitude as the energy increase, due to environmental distortion, or even larger. If the energy balance is critical, some tiny extra effects may be sufficient to tip the balance toward distortion.

In conclusion this semiquantitative calculation of polarization energies in AB compounds with $(ns)^2$-ions supports the assumption that $(ns)^2$-ions tend to distort their originally centrosymmetrical environment to become noncentrosymmetrical.

Acknowledgments

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