

Fifty years of Szigeti's dielectric theory – A review*

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Abstract. During the period 1949–1961 Szigeti published four seminal papers on the dielectric behaviour of crystals. Szigeti's theory is applicable to isotropic and anisotropic, ionic and covalent crystals with different structures. Szigeti's theory connects dielectric, spectroscopic and elastic properties. An important outcome of Szigeti's theory is the concept of the effective ionic charge (s). It is pointed out that s correlates with a number of physical properties and is a measure of ionicity of the interatomic bond. Since Szigeti's work, several theoretical models have been proposed to account for the fact that $s < 1$. These models provide an insight into the complex polarization mechanisms in solids. This review summarizes Szigeti's work and the work that followed; the implications and applications of Szigeti's theory are discussed. Some new results are also included.

Keywords. Polarization; dielectric properties; effective ionic charge; lattice vibrations.

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1. Introduction

The electric polarization P in a crystal is related to the applied electric field E by the relation

$$P = \alpha E, \quad (1)$$

where α is the polarizability. The dielectric constant ε is related to the polarizability through the relation

$$\varepsilon - 1 = 4\pi\alpha. \quad (2)$$

This relation does not take into account the internal field. When the internal field is included, we are led to the Clausius–Mosotti relation

*Dedicated to the memory of late Prof. P S Narayanan.

$$(\varepsilon - 1)/(\varepsilon + 2) = (4\pi/3)\alpha. \quad (3)$$

The Clausius–Mosotti equation is valid when the environment around every ion has tetrahedral symmetry as in the alkali halides. Further, it applies only to cubic crystals. The polarizability α is made up of two components, the atomic polarizability α_a arising out of the ionic displacements and the electronic polarizability α_e arising out of the displacement of the electron cloud relative to the nucleus. With proper substitution for α_a and α_e we get

$$[(\varepsilon_s - 1)/(\varepsilon_s + 2)] - [(\varepsilon_\infty - 1)/(\varepsilon_\infty + 2)] = (4\pi/3)\alpha_a, \quad (4)$$

where ε_s and ε_∞ are the static and high frequency dielectric constants. But this extended Clausius–Mosotti equation also does not work well and alternate theories have been proposed to account for the dielectric behaviour of solids. These theories are dependent on the details of the polarization mechanisms considered in each theory. Thus, assuming that the ions are rigid (non-deformable) and non-overlapping, Born and Mayer [1] obtained

$$\varepsilon_s = \varepsilon_\infty + (z^2 e^2 N)/\pi\mu\nu_t^2. \quad (5)$$

Here z is the valency, e the electron charge, N the number of molecules in unit volume and ν_t the transverse optical frequency. μ is the reduced mass given by

$$\mu^{-1} = m_1^{-1} + m_2^{-1}, \quad (6)$$

m_1 and m_2 being the masses of the positive and negative ions. Equation (5) is valid for an ionic crystal with two different ions having a single transverse optic infrared active mode. Agreement of eq. (5) with experiment is not satisfactory.

Nearly fifty years ago, a theory of the dielectric constant of ionic crystals was proposed by Szigeti through four seminal papers [2–5]. This is by far the most comprehensive theory. Though it was derived for ionic crystals like alkali halides, it is found to apply to partially ionic crystals, to triatomic crystals and also, to anisotropic crystals. The theory includes anharmonic effects and also relates the dielectric constant to the compressibility. Moreover, Szigeti’s theory was the starting point for the development of several models of dielectric polarization. The purpose of this article is to review Szigeti’s theory and discuss its implications and applications.

2. Szigeti’s theory: A

2.1 Szigeti’s first relation

Szigeti developed a theory which resulted in a relation between the dielectric constant and the lattice frequency. The derivation of the relation is to be found in Szigeti’s paper [2] and also in Born and Huang [6] and Brown [7]. Here, we shall note the main features of Szigeti’s theory. These are:

- (i) The ions are deformable and they overlap.
- (ii) The polarization in dielectric crystals has two parts: the infrared polarization and the ultraviolet polarization.
- (iii) While the ultraviolet polarization is the same as the electronic polarization, the infrared polarization has contributions from both electronic and atomic polarizations.
- (iv) The atomic and electronic polarizations are not independent but there is an interaction between them. This interaction is separated into short-range and long-range effects.
- (v) The total dipole moment M is split into two parts:

$$M = M_i + M_u, \quad (7)$$

where M_u is the contribution of the electronic oscillators with ultraviolet frequencies and M_i is the infrared part. M_i is written as

$$M_i = \sum_j \frac{\partial M}{\partial Q_j} Q_j, \quad (8)$$

where the Q_j 's are normal coordinates. The summation is over normal modes of infinite wavelength as only such waves contribute to macroscopic dielectric properties. It is to be noted that Szigeti included only first-order terms in the summation.

With these features and assumptions, Szigeti [2] obtained the following relation:

$$\varepsilon_s = \varepsilon_\infty + [(\varepsilon_\infty + 2)/3]^2 [s^2 (ze)^2 N / \pi \mu \nu_t^2]. \quad (9)$$

Equation (8) is known as Szigeti's first relation. The first term on the right-hand side (ε_∞) is the contribution of the ultraviolet polarization and the second is due to infrared polarization. Szigeti's relation (eq. (9)) contains two factors not present in Born's relation (eq. (5)); both arise out of the electronic contribution to the infrared polarization. The factor $[(\varepsilon_\infty + 2)/3]^2$ is due to the fact that the long-range interaction does not vanish for transverse waves. The other new factor is s which represents the short-range interaction of electronic and atomic displacements. The term sze is equivalent to replacing ze by an effective charge ze^* ; then $sze = ze^*$ and $s = (ze^*/ze)$. In subsequent literature, s has come to be known as the 'effective ionic charge' or the 'Szigeti charge'.

As Szigeti's theory was developed mainly for the alkali halides, we shall consider the values of s for the alkali halides calculated from eq. (9). For this purpose, it is convenient to rewrite eq. (9) as

$$s = (9\pi\mu/N)^{1/2} (\varepsilon_s - \varepsilon_\infty)^{1/2} (\varepsilon_\infty + 2)^{-1} (\nu_t/ze). \quad (10)$$

The value of s for some alkali halides calculated by Szigeti [2] are given in table 1. The input data ($\varepsilon_s, \varepsilon_\infty, \nu_t$) used by Szigeti was from earlier sources [8,9]. Values calculated by Lowndes and Martin [10] from their own more recent and accurate data are also included in table 1. The values in both sets are mutually consistent.

Table 1. Values of the effective ionic charge s and the anharmonic correction.

Crystal	s (eq. (10))		Anharmonic corrections (eqs (17), (18))	
	Szigeti [2]	Lowndes and Martin [10]	$G/(\epsilon_s - \epsilon_\infty)$	s'
LiF	0.87	0.81	0.0039	0.808
LiCl	–	0.79	0.0161	0.783
LiBr	–	0.73	–0.0150	0.735
LiI	–	–	–	–
NaF	0.93	0.83	0.0214	0.821
NaCl	0.74	0.77	0.0245	0.760
NaBr	0.69	0.74	0.0184	0.733
NaI	0.71	0.73	0.0178	0.723
KF	–	0.91	0.0310	0.895
KCl	0.80	0.81	0.0502	0.789
KBr	0.76	0.78	0.0015	0.755
KI	0.69	0.74	0.0921	0.705
RbF	–	0.95	–	–
RbCl	0.84	0.83	0.0512	0.808
RbBr	0.82	0.80	0.0638	0.774
RbI	0.89	0.77	0.0867	0.736
CsF	–	0.95	–	–
CsCl	0.84	0.85	–0.0570	0.874
CsBr	0.79	0.82	–0.0760	0.850
CsI	–	0.78	–0.0427	0.7964

A common feature in the s values is that they are significantly less than unity. Szigeti [2] himself pointed out that the deviation of s from unity could be due to a partial homopolar (partial ionic) character or due to interpenetration of the ions. In deriving eq. (9), a harmonic crystal was assumed as implied by eq. (8). Szigeti [3] qualitatively surmised that this may not affect the s values. However, he examined this aspect rigorously in 1959 [4]. These and other aspects will be considered in later sections.

2.2 Anharmonic correction to s

Szigeti [4] considered the effect of anharmonicity on s . For this, he expressed the dipole moment M as

$$M = \alpha_0 Q_0 + \sum_{ij} \beta_{ij} Q_i Q_j + \sum_{ijk} \gamma_{ijk} Q_i Q_j Q_k, \tag{11}$$

where the Q 's are the normal coordinates and α_0 , β_{ij} and γ_{ijk} are constants. Q_0 is the transverse optic infrared active mode. Here the first term contains the effect of displacement of ions and also the electronic distortions while the second and

third terms are due entirely to electronic deformation. Similarly, he expressed the potential energy W as

$$W = W_h + W', \quad (12)$$

$$W_h = (1/2) \sum_i \omega_i^2 Q_i^2, \quad (13)$$

and

$$W' = \sum_{ij} b_{ijk} Q_i Q_j Q_k + \sum_{ijkl} c_{ijkl} Q_i Q_j Q_k Q_l. \quad (14)$$

Here W_h represents the harmonic and W' the anharmonic terms. $(\omega_i/2\pi)$ is the frequency ν_i of the i th mode and b_{ijk} and c_{ijkl} are constants. While macroscopic polarization arises only out of long wavelength modes, the summation in eqs (13) and (14) involves normal modes of all wavevectors. W is the potential energy with respect to all forces arising from lattice displacements. Therefore,

$$W = \text{potential energy of lattice} + E_{\text{ext}} M. \quad (15)$$

where M and W are given by eqs (11) and (12) and E_{ext} is the external field. Writing the Hamiltonian and applying perturbation theory, Szigeti [4] showed that

$$\varepsilon_s - \varepsilon_\infty = \eta + G, \quad (16)$$

where η is the harmonic and G the anharmonic contributions. η is the second term in eq. (9) whereas G is a function of the two dielectric constants and the constants in eqs (11) and (14).

In a later paper, Szigeti [5] expressed G in terms of measurable quantities and obtained:

$$\frac{G}{(\varepsilon_s - \varepsilon_\infty)} = \frac{T\varepsilon_s}{(\varepsilon_s - \varepsilon_\infty)} \left[\frac{1}{\varepsilon_s} \left(\frac{\partial \varepsilon_s}{\partial T} \right)_P + \frac{1}{\varepsilon_s} \left(\frac{\partial \varepsilon_s}{\partial P} \right)_T \left(\frac{3\alpha}{\psi} \right) \right], \quad (17)$$

where α is the linear coefficient of thermal expansion, ψ the compressibility and T the temperature. s' , the Szigeti charge corrected for anharmonicity is given by

$$s' = s(1 - \delta)^{1/2}, \quad (18)$$

where δ is the anharmonicity correction $G/(\varepsilon_s - \varepsilon_\infty)$.

The importance of Szigeti's work lies in relating the anharmonic correction to experimentally measured quantities like thermal expansion coefficient and compressibility without assuming any detailed model for the anharmonic forces.

Szigeti [5] estimated the anharmonic correction $G/(\varepsilon_s - \varepsilon_\infty)$ only for three alkali halides (NaCl, KCl and LiF) as the required experimental data was available only for these crystals. From the results, Szigeti [5] concluded that the anharmonic correction (i) is very small, of the order of 10^{-2} , (ii) affects the s value by about 2% and (iii) enhances, though very slightly, the deviation of s from unity. Samara

[11] extended these calculations to crystals with CsCl structure. His results showed that the anharmonic correction $G/(\varepsilon_s - \varepsilon_\infty)$ is negative for these crystals and it reduces the difference between s and unity.

As mentioned, due to the availability of limited data, Szigeti [5] could estimate the anharmonic correction only for three alkali halides. Further, he did not report the value of s' . Recently, data on all the quantities in eq. (16) for several alkali halides have been compiled by Sirdeshmukh *et al* [12]. Using these data, the present authors have estimated the anharmonic correction $G/(\varepsilon_s - \varepsilon_\infty)$ and the corrected Szigeti charge s' from eqs (16) and (17) for a number of alkali halides. These results are included in table 1. It is seen that the anharmonic correction $G/(\varepsilon_s - \varepsilon_\infty)$ has a small value and the s' values are only slightly different from the s values. Thus, the neglect of anharmonicity in the derivation of Szigeti's first relation (eq. (10)) is not the cause of the difference between s and unity.

It can also be seen that the anharmonic correction has different signs for different crystals. Thus, it is negative for LiBr and the cesium halides and positive for the other alkali halides. The negative value is of significance. It is observed [11,13] that crystals with a negative anharmonic correction have a negative value for the temperature derivative of static dielectric constant.

2.3 Spectroscopic implication of the Szigeti relation

Lyddane *et al* [14] derived the following relation:

$$(\varepsilon_s/\varepsilon_\infty) = (\omega_l^2/\omega_t^2), \quad (19)$$

where ω_l and ω_t are the longitudinal and transverse optical phonon frequencies respectively. This relation is referred to as the Lyddane–Sachs–Teller (LST) relation. Combining the LST relation with Szigeti's relation (eq. (10)), we get

$$s^2 = (9\mu/4\pi N z^2 e^2)[\varepsilon_\infty/(\varepsilon_\infty + 2)^2][\omega_l^2 - \omega_t^2]. \quad (20)$$

This relation relates s with the splitting ($\omega_l^2 - \omega_t^2$) of the optical mode. This splitting is an essential consequence of Szigeti's relation. Mitra and Namjoshi [15] comment that 'no matter how one defines ionicity of a crystal, its only manifestation is in the splitting of the longitudinal and transverse optic phonon frequencies at $k \sim 0$ '.

2.4 Later developments

Although the term s in eq. (9) was attributed by Szigeti to the short-range interaction of electronic and atomic displacements, the fact remains that the term was introduced by Szigeti almost arbitrarily to bring about equality between the two sides of eq. (9). The value of s was not evaluated by Szigeti independently, but rather from eq. (9). An evaluation of s independently of Szigeti's relation was certainly desirable. Several models were developed to account for the s values and, more particularly, to account for the deviation of s from unity. These models are discussed in this section.

Yamashita [16] and Yamashita and Kurosawa [17] treated the problem by a quantum mechanical variation method. They calculated the ionic charge for LiF. Narasimhan [18] extended Yamashita's method to MgO. Yamashita's method has not found further application as it involves more parameters than can be evaluated from experimental data.

Szigeti [3] himself suggested that the mutual distortions of the ions due to their overlap could be a cause of the s values being <1 . Born and Huang [6] pointed out that such distortions would result in a 'distortion dipole moment' $m(r)$ and that this dipole moment would cause s to be <1 . However, the treatment of Born and Huang was qualitative. Lundquist [19] used the Heitler–London approach to evaluate the overlap distortion moment for NaCl.

Dick and Overhauser [20] reexamined Szigeti's theory. They pointed out that apart from the electronic polarization and polarization due to displacement of ions included in Szigeti's theory, it is necessary to include 'some further polarization'. Thus, they introduced the concepts of short-range interaction polarization and exchange charge polarization into the theory. These arise from charge redistributions which occur when ions move with resulting changes in electron overlap. Formulating their theory in terms of the shell model, Dick and Overhauser calculated the integrals S_{ij} necessary to estimate the exchange charge. Finally they obtained a 'generalized Szigeti relation':

$$s = (e'/e)[1 + (A\mu/e')(1 + A\lambda)^{-1}]. \quad (21)$$

Here e' , A , μ and λ are parameters occurring in the theory; these can be theoretically estimated for each crystal. The values of s calculated from eq. (18) are given in table 2. These values follow the same general trends as the original Szigeti (or Lowndes and Martin) values but are seen to be systematically larger and hence closer to unity. Dick and Overhauser concluded that the short-range interaction polarization and the exchange charge polarization are responsible for the deviation of s from unity.

Hanlon and Lawson [21] observed that the values of the Szigeti charge s of alkali halides lie on a smooth curve when plotted against the difference in the polarizabilities of the negative and positive ions. In order to explain this empirical observation, Hanlon and Lawson modified Szigeti's theory by including the contribution of a mechanical polarization. When an electric field is applied, each ion will be polarized in the direction of the field. But the ions will also move relatively closer. Their electron shells will mechanically repel one another, resulting in a relative shift of each electron cloud with respect to its nucleus. This shift corresponds to an additional polarization. In the positive ion, this mechanical polarization enhances the electrical polarization, but in the negative ion it detracts. Hanlon and Lawson showed that this mechanical polarization contributes to the value of s . Hanlon and Lawson's model led to the following relation:

$$(1 - s) = \frac{[f\mu\Omega_R^2(\alpha_0^- - \alpha_0^+)]/ze^2}{[1 - f\mu\Omega_R^2(\alpha_0^- - \alpha_0^+)]/z^2e^2}. \quad (22)$$

Here Ω_R is the resonance frequency, z the effective number of electrons contributing to the polarizability and f a theoretical parameter. s cannot be evaluated from

Table 2. Values of the Szigeti charge s obtained from different models.

Crystal	s									
	a	b	c	d	e	f	g	h	i	j
LiF	0.81	0.91	0.87	0.77	0.638	0.63	1.01	0.75	0.82	
LiCl	0.79	0.92	–	–	–	–	1.13	0.66	0.78	
LiBr	0.73	0.91	–	–	–	–	1.15	0.63	0.74	
LiI	–	0.91	–	–	–	–	–	–	–	
NaF	0.83	0.93	0.91	0.96	0.69	0.73	0.96	0.83	0.82	0.77
NaCl	0.77	0.91	0.74	0.74	0.66	0.61	0.97	0.77	0.76	0.78
NaBr	0.74	0.89	0.70	0.69	–	0.60	1.02	0.74	0.74	0.78
NaI	0.73	0.89	0.69	0.64	–	0.63	1.04	0.70	0.70	0.83
KF	0.91	0.98	–	–	–	–	0.91	0.97	0.88	0.82
KCl	0.81	0.93	0.85	0.83	0.71	0.69	0.83	0.91	0.78	0.85
KBr	0.78	0.93	0.77	0.78	0.67	0.58	0.88	0.86	0.75	0.86
KI	0.74	0.91	0.69	0.72	0.67	0.54	0.72	0.89	0.71	0.86
RbF	0.95	1.05	–	–	–	–	0.96	1.00	0.93	0.85
RbCl	0.83	0.95	0.91	0.86	–	0.73	0.91	0.93	0.81	0.89
RbBr	0.80	0.92	0.83	0.80	–	0.66	0.86	0.92	0.77	0.90
RbI	0.77	0.93	–	0.75	–	0.68	0.85	0.91	0.73	0.91
CsF	0.95	–	–	–	–	–	1.12	0.92	0.93	
CsCl	0.85	–	–	0.91	–	0.60	0.93	0.93	0.83	
CsBr	0.82	–	–	0.83	0.57	0.63	0.88	0.91	0.79	
CsI	0.78	–	–	–	0.67	0.51	0.86	0.84	0.74	

(a) Expt. values, Lowndes and Martin [10]; (b) Dick and Overhauser [20]; (c) Hanlon and Lawson [21]; (d) Havinga [22]: eq. (23); (e) Havinga [22]: eq. (24); (f) Havinga [22]: eq. (25); (g) Goyal *et al* [28]: (LM); (h) Goyal *et al* [28]: (SM); (i) Goyal *et al* [28]: (TSM); (j) Mahan [29], Michihiro *et al* [30].

this relation directly. But, Hanlon and Lawson plotted the known values of $(1 - s)$ against the right-hand-side assuming values of z and f/z . The plot with $z = 4$ and $f/z = 0.53$ is shown in figure 1. Most of the data points lie on a linear plot. Introducing these values of z and f/z in the right-hand side of eq. (22), Hanlon and Lawson recalculated s ; these s values are included in table 2.

Havinga [22] critically examined the model of Dick and Overhauser [20]. He ignored the ‘exchange charge’ part in Dick and Overhauser’s model and, further, converted the various model parameters into experimental properties. Thus, he obtained the following ‘new expressions’ for the Szigeti charge s :

$$(1 - s)^2 = [(\epsilon_s + 2)/(\epsilon_\infty + 2)][\mu\omega_t^2/z^2 e^2](\alpha_+^{\text{free}} - \alpha_-^{\text{free}} - \alpha_\infty), \quad (23)$$

$$(1 - s)^2 = \frac{[(\epsilon_\infty - 1)/(\epsilon_\infty + 2)]\gamma + [3/(\epsilon_\infty + 2)^2](\partial\epsilon_\infty/\partial T)}{[(\epsilon_s - 1)/(\epsilon_s + 2)]\gamma + [3/(\epsilon_s + 2)^2](\partial\epsilon_s/\partial T)}, \quad (24)$$

and

$$(1 - s)^2 = \frac{[(\epsilon_\infty - 1)/(\epsilon_\infty + 2)]\beta + [3/(\epsilon_\infty + 2)^2](\partial\epsilon_\infty/\partial P)}{[(\epsilon_s - 1)/(\epsilon_s + 2)]\beta + [3/(\epsilon_s + 2)^2](\partial\epsilon_s/\partial P)} \quad (25)$$

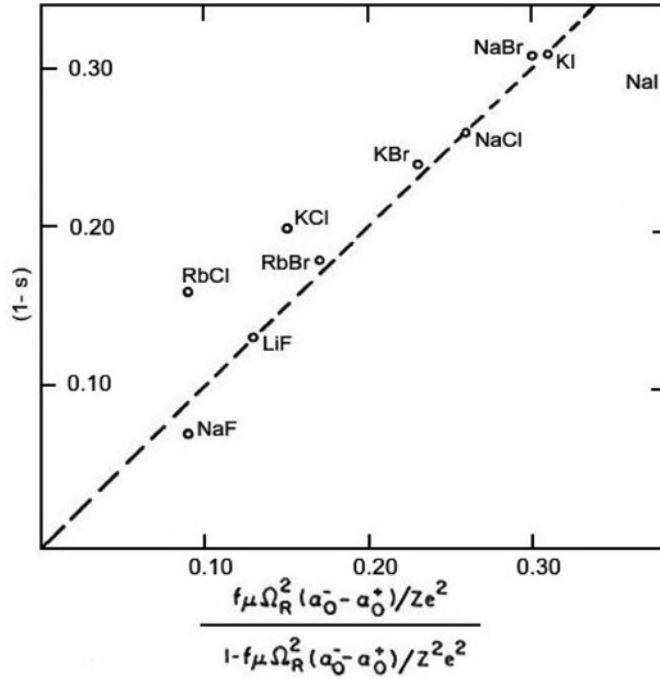


Figure 1. Plot of $(1 - s)$ vs. the right-hand side of eq. (22) with $z = 4$ and $f/z = 0.53$.

Here γ is the volume coefficient of thermal expansion and β is the negative of compressibility. Having calculated the s values from eq. (23) using literature values for the polarizabilities. Their values of s are given in table 2. Due to limitation of data on pressure and temperature derivatives of the dielectric constants, Havinga tested eq. (24) only on NaCl and KCl and eq. (25) only on NaCl. The present authors have calculated s values from eqs (24) and (25) for several alkali halides taking recent data from Sirdeshmukh *et al* [12]. These values (table 2; columns d, e, f) are substantially less than the s values from most other sources.

Hardy [23] critically examined the assumptions in the model of Dick and Overhauser [20]. He assumed that the change in charge density due to ionic distortion is proportional to that predicted from the overlap of the free ion functions. The most important contribution made by Hardy [23] is that he split the dipole moment $m(r)$ into two parts $m_+(r)$ and $m_-(r)$ centred on the positive and negative ions respectively. The general expression for these dipole moments is

$$m_{\pm} = \frac{q_{\text{exc.}} r_{\pm}}{2} = |e| \sum_{ij} S_{ij}^2 r_{\pm}, \quad (26)$$

where

$$\sum_{ij} S_{ij}^2 \propto \lambda R_0 \exp(-R_0/\rho). \quad (27)$$

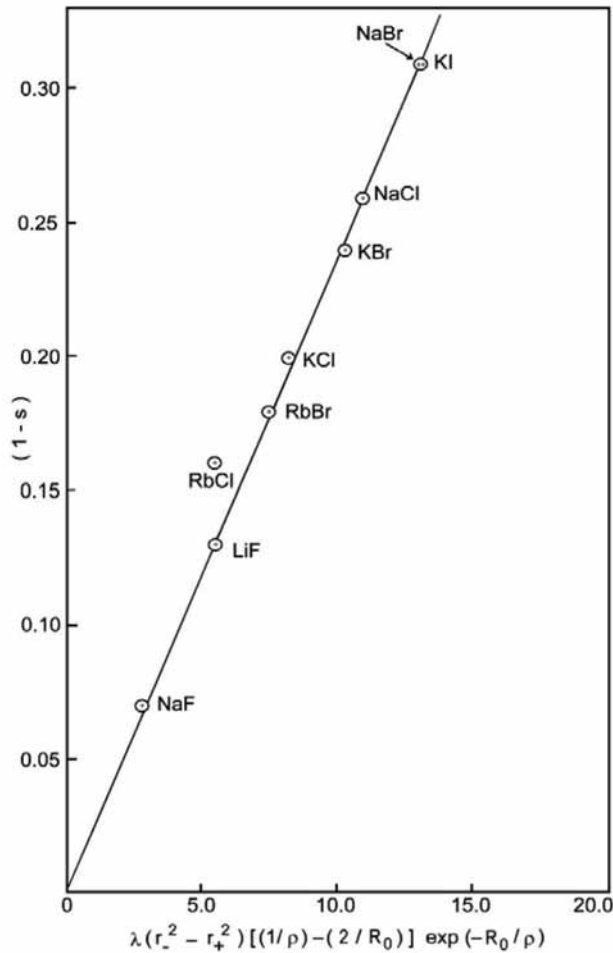


Figure 2. Plot of $(1 - s)$ vs. the right-hand side of eq. (28).

Combining eqs (26) and (27), Hardy [23] finally obtained

$$(1 - s) \propto \lambda(r_-^2 - r_+^2)[(1/\rho) - (2/R_0)] \exp(-R_0/\rho). \quad (28)$$

In the above, S_{ij} is an integral appearing in Dick and Overhauser's theory, r_- and r_+ are the ionic radii, R_0 the interionic distance, and λ and ρ are constants in the Born repulsion term. Hardy showed that the plot of $(1 - s)$ against the right-hand side is linear (figure 2).

The concept of the deformation dipole moment originally introduced to explain the Szigeti charge values was applied by Hardy to the problem of lattice dynamics of alkali halide crystals. Hardy [24] included the interactions due to the deformation dipole moment in the dynamical matrix for KCl to obtain the dispersion curves. This method was applied to study the lattice dynamics of several other alkali halide crystals with NaCl and CsCl structures [25,26].

Mitskevitch [27] considered the effect of multipole interactions on ionic distortions and hence on the values of s . The monopole–dipole interactions are cancelled but the monopole–hexadecapole interaction makes a significant contribution. Values of s calculated by Mitskevitch for some alkali halides from such an interaction agree well with the experimental values of s .

Goyal *et al* [28] examined the close dependence of the effective ionic charge upon the lattice vibration model. They derived expressions for s corresponding to the Lundquist (LM), simple shell (SM) and three-body shell (TSM) models. The values are given in table 2. They are of the same order and differ only slightly from those calculated by Lowndes and Martin [10] from Szigeti's relation (eq. (10)).

In recent years, Mahan [29] has revived the deformation dipole model originally introduced by Hardy in the 1960s. Mahan [29] made *ab initio* calculations of the polarizabilities of alkali ions and used them to calculate the refractive index and the effective ionic charge by employing improved 'computational technology'.

Mahan [29] put down the deformation dipole moment \bar{p}_l^μ as

$$\bar{p}_l^\mu = \sum_{\nu=1}^3 \bar{\gamma}_l^{\mu\nu}(R_k) e Z_k u_k^\nu, \quad (29)$$

where $\bar{\gamma}_l^{\mu\nu}$ is the deformation dipole tensor of the ion l , R_k the relative site vector between ions l and k , z_k the valence and u_k^ν the relative displacement of ion k . Mahan derived the perturbation equations for the deformation dipole tensor by the combined use of self-consistent treatment of local density approximation and the spherical solid model. The effective ionic charge s is calculated from

$$s = (1 - \tau) \quad (30)$$

and

$$\tau = 2(\gamma_l + 2\gamma_t). \quad (31)$$

Here γ_l and γ_t are the longitudinal and transverse components of the tensor. Mahan [29] calculated the values of s for alkali halides excluding the iodides. Recently, Michihiro *et al* [30] extended Mahan's method to the alkali iodides. The resulting s values are included in table 2. Mahan concluded that the deformation dipole model can explain the origins of the deviation of s from unity.

The attempts described above have introduced some sophistication into Szigeti's theory and have provided a deeper insight into the polarization mechanisms. However, as far as the effective charge is concerned, the values given by the simple Szigeti relation have remained essentially unaltered.

3. Aspects of the Szigeti charge

3.1 Values of s for various crystals

The most important aspect of Szigeti's theory is the concept of the effective ionic charge s . This is also called the Szigeti charge and is often denoted by q^* . Though Szigeti [2] had mainly the alkali halides in view, he evaluated the value of s for

Table 3. Values of the Szigeti charge s for crystals with different structures.

Crystal	s	Ref.	Crystal	s	Ref.
<i>NaCl structure</i>			<i>Diamond structure</i>		
AgCl	0.69	a	C	0	h
AgBr	0.68	a	Si	0	h
MgO	0.60	b	Ge	0	h
CaO	0.64	b	<i>ZnS structure</i>		
SrO	0.78	b	GaP	0.58	h
BaO	0.66	b	GaAs	0.51	h
NiO	0.84	c	GaSb	0.33	h
CoO	0.89	c	InP	0.68	h
MnO	1.08	c	InAs	0.56	h
CaS	0.41	d	InSb	0.42	h
SrS	0.58	e	ZnS	0.85	h
BaS	0.49	e	ZnSe	0.71	h
<i>CsCl structure</i>			ZnTe	0.53	h
TlCl	0.87	a	CdS	1.00	h
TlBr	0.84	a	CdSe	0.71	h
<i>FeS₂ structure</i>			CdTe	0.74	h
FeS ₂		f	<i>Rutile structure</i>		
MnTe ₂	0.62	f	MgF ₂	0.83	i
<i>Sr(NO₃)₂ structure</i>			TiO ₂	0.58	j
Pb(NO ₃) ₂	0.84	g	GeO ₂	0.54	j
Sr(NO ₃) ₂	1.04	g	SnO ₂	0.57	j
Ba(NO ₃) ₂	0.71	g			

(a) Lowndes and Martin [10]; (b) Sirdeshmukh and Sirdeshmukh [32]; (c) Plendl *et al* [33]; (d) Sirdeshmukh and Reddy [34]; (e) Sirdeshmukh [35]; (f) O'Nari *et al* [36]; (g) Sirdeshmukh [37]; (h) Mitra and Marshall [31]; (i) Sirdeshmukh [38]; (j) Gervais [39].

several other cubic diatomic crystals like TlCl, MgO and ZnS, triatomic crystals like CaF₂ and anisotropic crystals like TiO₂. In the same spirit, the Szigeti charge has been evaluated by several workers for crystals belonging to different structures. Mitra and Marshall [31] quoted values for the fully covalent diamond-type crystals and to several partially covalent crystals like ZnS. s values for several crystals are given in table 3.

The experimental quantities needed for the calculation of the Szigeti charge are ϵ_∞ , ϵ_s and ν_t . Values of ϵ_∞ are generally very accurate. But uncertainties do exist in the values of ϵ_s and ν_t which can create uncertainties in s . Thus Havinga [22] reported values of 0.79 and 0.89 for s for RbI using different values of ϵ_s . Similarly, s values of 0.94 and 0.87 were reported by Samara [40] for PbF₂ using different values of ν_t . Thus an uncertainty of 5–10% can exist in the reported s values.

3.2 Szigeti charge and ionicity

It can be seen from tables 1 and 3 that, in general, $s \leq 1$. Some views regarding the factors that contribute to the difference $(1 - s)$ have been discussed in §2.4.

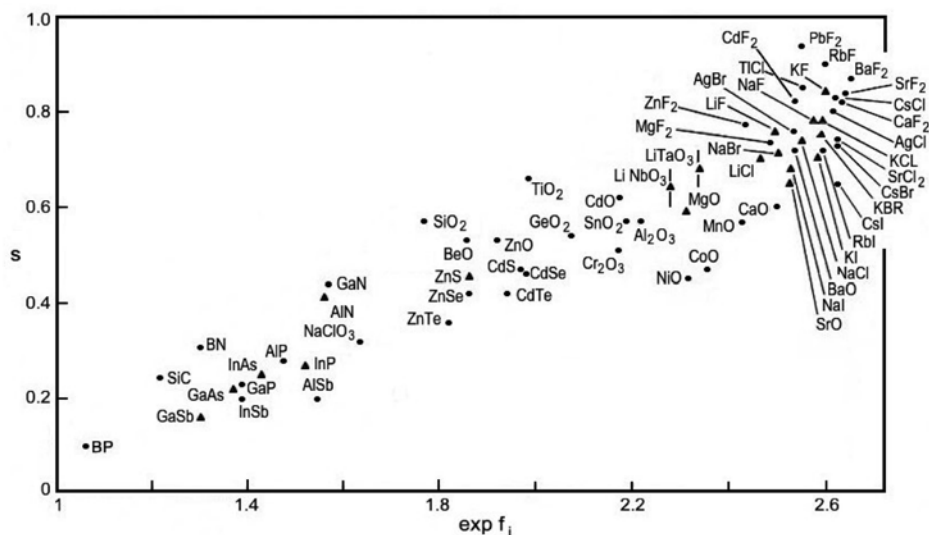


Figure 3. Plot of s vs. $\exp f_i$.

Szigeti [2] himself suggested that one of the factors could be that ‘the bond has a partial homopolar character’ but he did not pursue this possibility in any of his later papers. However, from time to time, the view has been expressed that the Szigeti charge is a measure of the ionicity of the bond in the crystal [15,36,41,43].

There are several measures of the ionicity. A commonly employed measure is the Phillips ionicity f_i [44]. Phillips plotted f_i against an effective charge S and obtained a linear plot. However, the effective charge S used by Phillips has a different definition and, further, he considered only crystals with the zinc blende structure. Gervais [39] examined the correlation of f_i and the Szigeti charge s by plotting s against $\exp(f_i)$ for over 60 crystals belonging to several structures. The plot (figure 3) was linear with data points evenly scattered around the straight line. Thus, the Szigeti charge s can be considered as a measure of ionicity of the bond.

3.3 Empirical relation between the Szigeti charge and physical properties of crystals

Apart from being an ionicity parameter, the Szigeti charge s is now considered an independent physical entity and correlations have been proposed between s and several physical properties. Some of them are discussed in this section.

3.3.1 s and interionic distance r : Ram Niwas *et al* [45] plotted $\log s$ against $\log r$ and obtained linear plots (figure 4) for each ion. They proposed the relation

$$s = kr^m, \tag{32}$$

where m is 0.5 for all plots and the constant k has a different value for each ion. From the plots it is seen that k increases with the size of the anion. Lowndes and

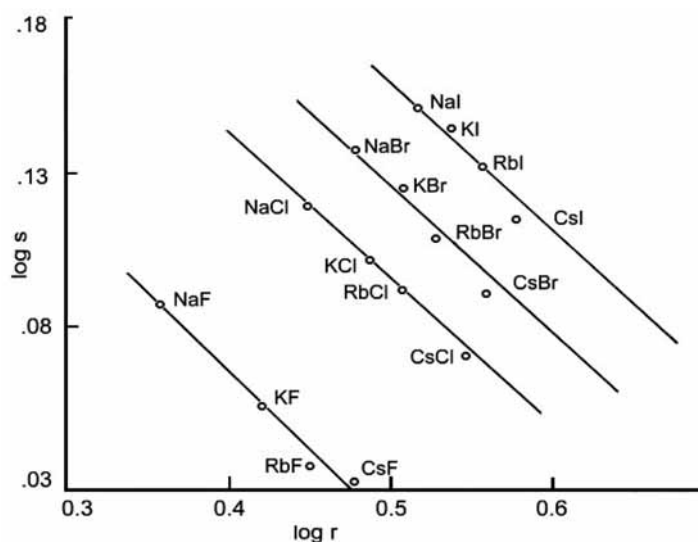


Figure 4. Plots of $\log s$ vs. $\log r$.

Martin [10] found that a plot of s and the radius ratio (r_+/r_-) for the alkali halides is a smooth curve (figure 5) with a separate curve for each halogen (or alkali ion). Koh [43] obtained linear s vs. (r_-/r) plots (figure 6). Assuming equations of the type

$$s = a(r^-/r) + b, \quad (33)$$

Koh obtained values of a and b for each cation.

3.3.2 s and polarizabilities: Hanlon and Lawson [21] plotted s against the polarizability difference ($\alpha_0^+ - \alpha_0^-$) for the alkali halides and obtained a smooth curve (figure 7) in the form of a hyperbola. Sirdeshmukh [46] used this curve to estimate values of s for the lithium halides which were not otherwise known at that time. On the other hand, Mitra and Marshall [31] found that the s vs. $(\alpha_0^+ - \alpha_0^-)$ plot is linear (figure 8) for the II–VI and III–V compounds with ZnS structure.

3.3.3 s and thermal expansion: Sirdeshmukh [46] proposed the following relation between s and the linear coefficient of thermal expansion α :

$$\alpha s^2 = \text{constant}. \quad (34)$$

This relation holds well in the case of the alkali halides with NaCl structure. Earlier, Megaw [47] proposed the relation

$$\alpha q^2 = \text{constant}. \quad (35)$$

Here q is the ‘electrostatic share’ given by the ratio of ionic charge ze to the coordination number C of an ion. Thus eq. (35) becomes

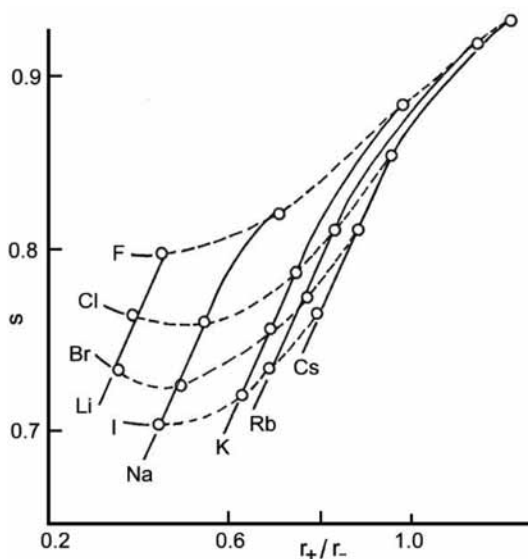


Figure 5. Plots of s vs. (r_+/r_-) .

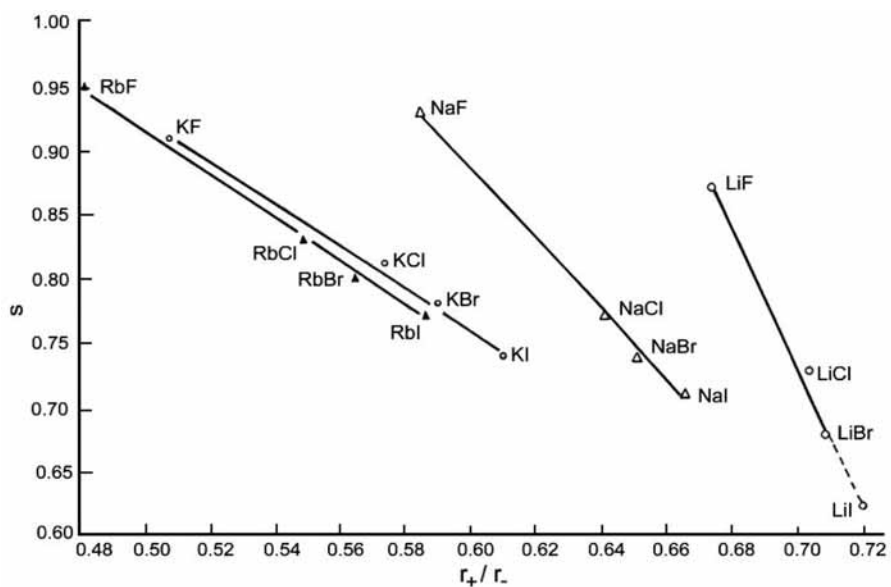


Figure 6. Plots of $\log s$ vs. (r_-/r) .

$$(\alpha z^2 e^2 / C) = \text{constant}. \quad (36)$$

This relation explains the difference in the thermal expansion of crystals with different valencies. Sirdeshmukh [46] pointed out that, in view of Szigeti's theory, eq. (36) reduces to eq. (34).

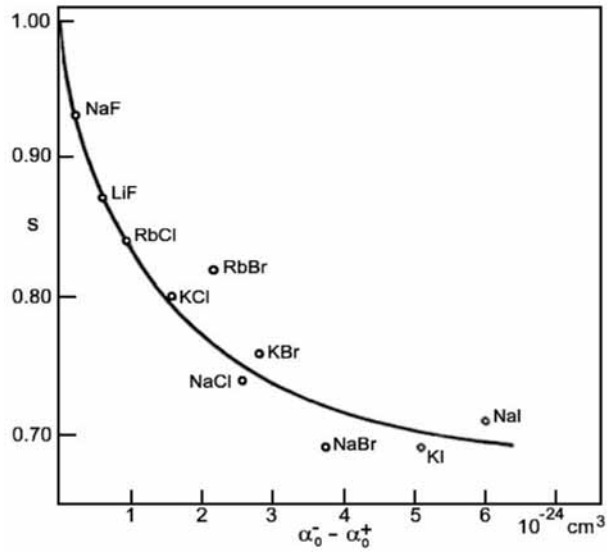


Figure 7. Plot of s vs. $(\alpha^- - \alpha^+)$ for alkali halides.

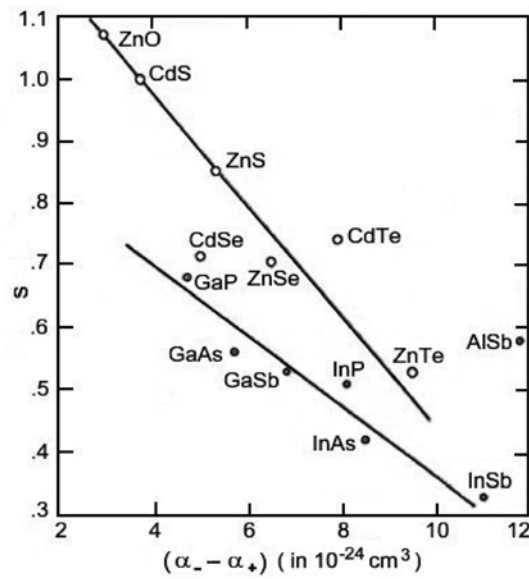


Figure 8. Plots of s vs. $(\alpha^- - \alpha^+)$ for II-VI and III-V compounds.

From rigorous lattice dynamics, Mitra [48] derived the relation

$$\gamma_t = \frac{(V_a/z^2)(\partial f/\partial V_a) - (4\pi/3)(s^2/V_a)}{(2f/z^2) - (8\pi^2/3)(s^2/V_a)}. \quad (37)$$

Here γ_t is the transverse optical Gruneisen parameter, V_a the unit cell volume, z

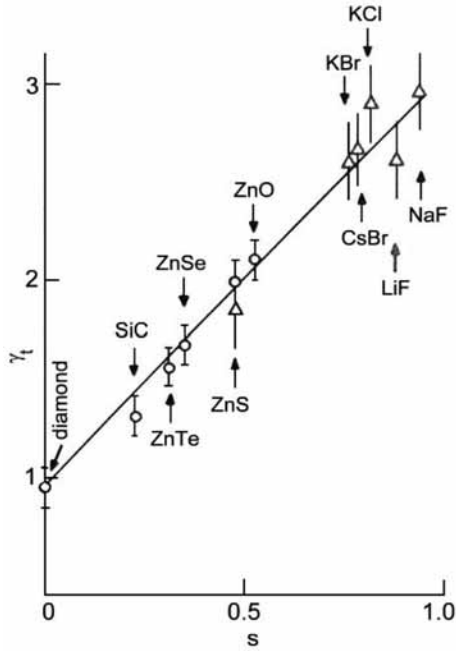


Figure 9. Plot of s vs. γ_t .

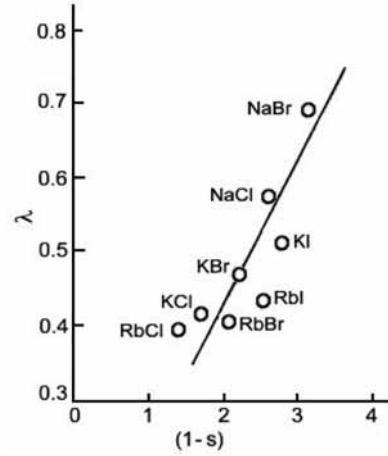


Figure 10. Plot of s vs. λ for alkali halides.

the valency and f the force constant. Mitra [50] argued that the first term in the numerator does not vary much from crystal to crystal and the second term in the denominator is very much smaller than the first term. Hence γ_t should correlate with s . A linear plot between γ_t and s is shown (figure 9) for a variety of crystals like Ge, Si, II–VI, III–V compounds and the alkali halides.

3.3.4 s and the strain polarizability constant λ : The strain polarizability constant λ is defined as

$$\lambda = 1 - (6n\rho)(n^2 + 2)^{-1}(n^2 - 1) - 1(\partial n/\partial \rho). \quad (38)$$

Here n is the refractive index and ρ the density. Burstein and Smith [49] suggested that qualitatively λ is a measure of homopolarity having a large value (~ 1) for diamond and smaller values (0.5) for the ionic alkali halides. Since s is a measure of ionicity, Bansigir [50] looked for a correlation between s and λ . Plotting s against λ for several alkali halides, he obtained a linear plot (figure 10).

3.3.5 s and the hyperfine coupling constant A : The hyperfine coupling constant (hfc) A of a crystal doped with ions can be theoretically estimated. It has been established that A is related to the degree of covalency in the bonding in the host lattice. Motida [51] calculated the hfc for a number of divalent crystals doped with Mn^{++} ions and found that the plot of A and $(1 - s)$ (figure 11) was linear. A linear plot was also obtained for $(1 - s)$ and A of alkali halides doped with Cr^+ ions.

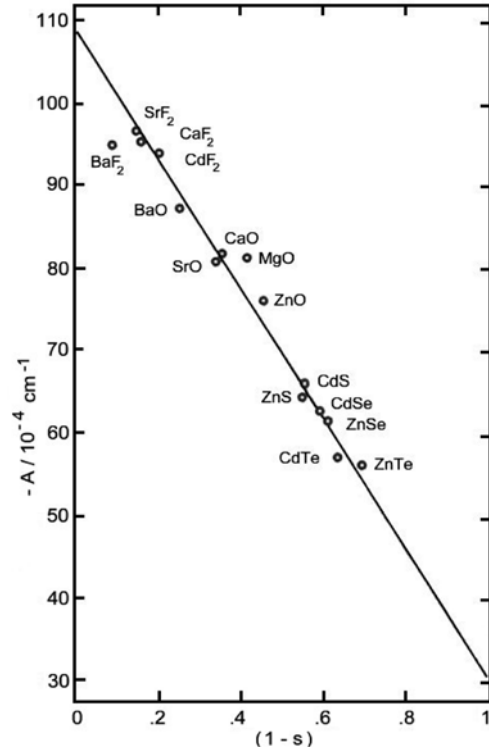


Figure 11. Plot of hfc constant A vs. $(1 - s)$ for Mn^{2+} -doped divalent compounds.

3.3.6 s and the microhardness H : Sirdeshmukh *et al* [52] calculated the Gilman–Chin parameter (H/C_{44}) for a number of halides, chalcogenides and carbides with NaCl structure; H is the microhardness and C_{44} the shear elastic constant. Examining the systematics in the (H/C_{44}) values, they found that the (H/C_{44}) vs. s^2 plot is hyperbolic (figure 12). On this basis, they suggested the relation

$$(H/C_{44})s^2 = \text{constant.} \quad (39)$$

3.3.7 s and plasma energy: Lawaetz [53] proposed the following empirical relation between the Sziget charge s and the plasma energy $\hbar\omega_P$:

$$s = C/\hbar\omega_P, \quad (40)$$

where C is a parameter occurring in the Phillip’s theory of ionicity [44].

3.3.8 s and energy of migration: Michihiro *et al* [30] pointed out that the activation energy Em for the cation migration in alkali halides shows an increase with the value of the Sziget charge; for cation migration smaller effective charge is more favourable. Since in the deformation dipole model (§2.4), the Sziget charge is

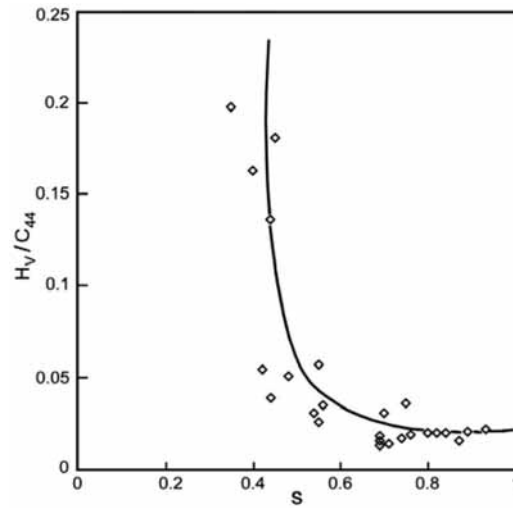


Figure 12. Plot of H vs. s for crystals with NaCl structure.

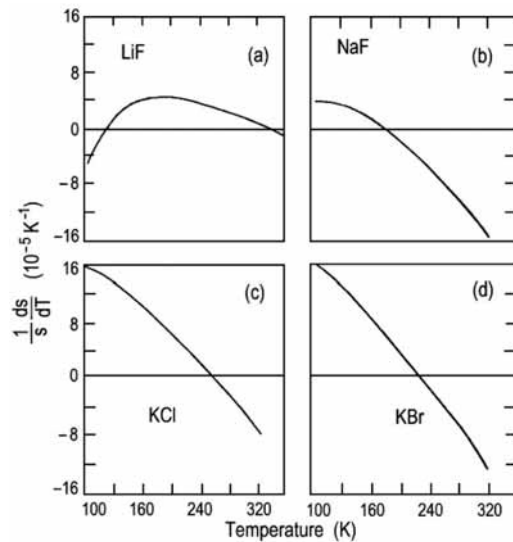


Figure 13. Temperature dependence of $(1/s) (ds/dT)$ for some alkali halides.

derived from the components of the deformation dipole tensor, Michihiro *et al* [30] explained the role of the deformation dipole tensor in the ease of cation migration.

3.4 Temperature variation of s

By differentiating s in eq. (10) with respect to the temperature, Kim *et al* [54] obtained

Table 4. Experimental and calculated values of $(V/s)(ds/dV)$.

Crystal	$(V/s)(ds/dV)$ Expt. ^a	Theoretical ^b			
		Shell model	Lawaetz model	Exchange charge model	Deformation dipole model
LiF	0.55	0.31	0.25	0.45	0.56
NaCl	0.63	0.40	0.32	0.45	0.96
KCl	0.52	0.29	0.31	0.73	0.82
KBr	1.03	0.32	0.42	0.93	1.09
KI	0.99	0.41	0.46	1.14	1.29
RbCl	0.47	0.19	0.46	0.68	0.81
RbBr	0.42	0.21	0.49	0.81	0.96
RbI	0.87	0.32	0.47	1.07	1.27

^aCalculated from eq. (43) by Shanker *et al* [58]; ^bModel-based calculations by Shanker *et al* [58].

$$(1/s)(ds/dT) = (3/2)\alpha + (1/\omega_t)(d\omega_t/dT) + (1/2)(1/\varepsilon_s - \varepsilon_\infty) \times [(\partial\varepsilon_s/\partial T) - (\partial\varepsilon_\infty/\partial T)] - (1/\varepsilon_\infty + 2)(\partial\varepsilon_\infty/\partial T). \quad (41)$$

Here, z is assumed to be 1, i.e., the equation applies to alkali halides. The results of the calculations for four alkali halides are shown in figure 13. The characteristic features are seen in the case of LiF. At low temperature $(1/s)(ds/dT)$ is negative. With increasing temperature, the value increases to become positive, passes a peak and becomes negative. The derivative, $(1/s)(ds/dT)$ may be written as

$$(1/s)(ds/dT) = (1/s)(\partial s/\partial T)_V + (1/s)(\partial s/\partial V)_T(3\alpha V). \quad (42)$$

The first term is due only to change in temperature and the second represents change due to thermal expansion. The net value of $(1/s)(ds/dT)$ is due to the result of the two competing contributions at different temperatures.

3.5 Pressure variation of s

Attempts to estimate the pressure (or volume) variation of s were made by Jones [55], Barron and Batana [56], Mitra and Namjoshi [15], and Batana and Faour [57]. The starting point in all these works is the differential form of eq. (10):

$$(V/s)(ds/dV) = 0.5 - \gamma_t - V(\partial\varepsilon_\infty/\partial V)[(\varepsilon_\infty + 2)^{-1} + (1/2)(\varepsilon_s - \varepsilon_\infty)^{-1}] + (1/2)V(\varepsilon_s - \varepsilon_\infty)^{-1}(\partial\varepsilon_s/\partial V). \quad (43)$$

The results obtained by them were provisional as they used theoretical values for the mode Gruneisen parameter γ_t .

Shanker *et al* [58], on the other hand, calculated γ_t from the experimental data of Lowndes and Rastogi [59] on temperature variation of the transverse optical phonon

frequency. Using these experimental γ_t values, they calculated $(V/s)(ds/dV)$ from eq. (43). These values of $(V/s)(ds/dV)$ are given in table 4. Shanker *et al* [58] also calculated $(V/s)(ds/dV)$ from various dielectric models. These values are also given in table 4. The data given in table 4 reveal the following features:

- (i) The experimental as well as model-based values of $(V/s)(ds/dV)$ are positive without exception. This implies that the decrease in crystal volume due to pressure increases overlap and distortion of ions, thereby causing a decrease in the effective ionic charge.
- (ii) The values of $(V/s)(ds/dV)$ obtained from the shell model and the Lawaetz model [53] are systematically smaller than experimental values, almost by a factor of 1/2.
- (iii) The values obtained from the exchange charge model and the deformation dipole model are comparable with each other and with the experimental values.

3.6 Szigeti charge of mixed crystals

The composition dependence of physical properties of mixed crystals differs from property to property and from system to system. Using experimental data on ϵ_s , ϵ_∞ , N and ν_t , the Szigeti charge s has been calculated as a function of composition for a few mixed crystal systems having NaCl structure. The conclusions from these studies are shown in table 5.

As shown in table 5, the composition dependence is linear in all cases. It may be noted that in the KCl–KBr system, the composition dependence is linear when the frequency data of Ferraro *et al* [65] is used while it is non-linear with the data of Fertel and Perry [66]. Thus, the frequency data plays an important role.

4. Szigeti's theory: B

4.1 Szigeti's second relation

Born and Huang [6] have given a historical account of the development of relations between compressibility and the infrared absorption frequency of crystals. Szigeti [3] also developed such a relation as a complement to his first relation (Sec. 2).

Szigeti [3] expressed the changes in the electronic configuration in terms of a dipole moment and 'local distortions'. The change in internal energy δW is expressed as a sum of two parts

$$\delta W = \delta V + \delta\Phi, \quad (44)$$

where V is that part of the electrostatic interaction energy which is obtained if the charge and polarization of each ion is replaced by a point charge and a point dipole placed in its centre. $\delta\Phi$ contains all the rest of the energy change: that part of the electrostatic interaction which is not included in δV , the van der Waals and repulsive energies and also the homopolar interaction energy, if any. In addition,

Table 5. Composition dependence of Szigeti charge in mixed crystals.

System	Observed composition dependence	Ref.
NiO–CoO	Linear	Gielisse <i>et al</i> [60]
NaCl–NaBr	Linear	Shanker and Jain [61]
KBr–KI	Linear	Shanker and Jain [61]
KCl–KBr	Linear using frequency data from Ferraro <i>et al</i> [65]	Sirdeshmukh <i>et al</i> [62]
	Non-linear using frequency data from Fertel and Perry [66]	
RbCl–RbBr	Linear	Sathaiah and Sirdeshmukh [63]
KCl–RbCl	Linear	Sinha and Shankar [64]

the self-energy of each ion is also altered due to the distortion of its electron cloud; this effect is also included in $\delta\Phi$.

Using derivatives of the terms in eq. (44) with respect to the interionic distance and replacing the total crystal energy terms W , V and Φ , for convenience by the corresponding terms w , v and ϕ for an ion pair, eq. (44) is rewritten as

$$(dw/dr) = (dv/dr) + (d\phi/dr). \quad (45)$$

Finally, considering the Coulomb and nearest neighbour short-range interactions, Szigeti [3] obtained the relation

$$(1/\psi) = (r^2/3V_a)[(\epsilon_s + 2)/(\epsilon_\infty + 2)]\mu(2\pi\nu_t)^2. \quad (46)$$

Here, ψ is the compressibility, r the interionic distance, V_a the volume per ion pair and the other symbols have already been defined. Equation (46) is known as Szigeti's second relation.

4.2 Application to alkali halides

Szigeti [3] applied eq. (46) to several alkali halides with NaCl and CsCl structures. The values of $(\psi_{\text{calc}}/\psi_{\text{obs}})$ for the alkali halides are given in table 6. ψ_{calc} is the theoretically calculated value and ψ_{obs} is the experimentally observed value. As expected, the values of $(\psi_{\text{calc}}/\psi_{\text{obs}})$ are close to unity but there are slight deviations which differ from crystal to crystal. Szigeti's values are based on old room temperature data [9] on ψ_{obs} . Values of $(\psi_{\text{calc}}/\psi_{\text{obs}})$ based on new, more accurate and low temperature data are also included in column 3 of table 6. These values are more evenly close to unity. In particular, RbI which showed the maximum deviation in Szigeti's value now falls in line with the other crystals.

As mentioned in §4.1, Szigeti [3] had considered only nearest-neighbour (nn) interactions in deriving eq. (46). Lowndes and Martin [10] considered the effect of including the next-to-nearest-neighbour (nnn) interactions. For this, they expressed the total energy as

Table 6. Values of $(\psi_{\text{calc}}/\psi_{\text{obs}})$ for alkali halides.

Crystal	$(\psi_{\text{calc}}/\psi_{\text{obs}})$				
	a	b	c	d	e
LiF	1.0	0.90	1.53	1.27	0.92
LiCl	–	1.17	1.66	1.36	1.03
LiBr	–	–	–	–	1.06
NaF	0.83	0.94	1.43	1.06	0.96
NaCl	0.99	1.00	1.21	1.09	1.04
NaBr	1.13	1.06	1.23	1.11	1.00
NaI	1.05	1.15	1.24	1.14	0.98
KF	–	0.97	1.46	0.97	0.87
KCl	0.96	0.98	1.06	1.04	1.01
KBr	0.95	0.99	1.01	0.97	0.99
KI	0.99	0.91	1.04	1.02	0.96
RbF	–	–	–	–	0.71
RbCl	0.89	1.04	1.06	0.97	0.90
RbBr	0.83	1.01	1.02	0.97	0.98
RbI	0.66	1.00	1.02	0.95	0.95
CsCl	0.87	–	–	–	–
CsBr	0.87	–	–	–	–

a: Eq. (46), ψ_{obs} at RT; Szigeti [3]; b: eq. (46), ψ_{obs} at low temperature; Lowndes and Martin [10]; c: ψ_{calc} including nnn interaction; Lowndes and Martin [10]; d: ψ_{calc} including angle-dependent forces; Lowndes and Martin [10]; e: ψ_{calc} from shell model: Roy *et al* [67].

$$W = W_{\text{nn}} + W_{\text{nnn}} + W_{\text{M}}, \quad (47)$$

where W_{M} is the Madelung term and the meaning of the other terms is self-explanatory. With this, they got the value

$$(\psi_{\text{calc}}/\psi_{\text{obs}}) = 1 + (DW_{\text{nn}})/[D(W_{\text{M}} + W_{\text{nnn}})], \quad (48)$$

where the operator D is given by

$$D = (1/9r)(\partial^2/\partial r^2) - (2/9r)(\partial/\partial r). \quad (49)$$

The values of $(\psi_{\text{calc}}/\psi_{\text{obs}})$ from eq. (48) are given in column 4 of table 6. They are, expectedly, larger than unity but in several cases the difference is too large. Szigeti [3] had neglected any effect of angular (homopolar) forces. Lowndes and Martin [10] considered this effect also and obtained a correction term

$$(1/\psi_{\text{L}}) = (1/\psi_{\text{s}}) + (C_{44} - C_{12}), \quad (50)$$

where ψ_{L} is the revised value, ψ_{s} the value from eq. (46) and C_{12} and C_{44} the elastic constants. The values of $(\psi_{\text{L}}/\psi_{\text{obs}})$ are given in column 5 of table 6. These are closer to the experimental values than the values from eq. (48).

Roy *et al* [6] used the shell model including the many-body interactions. Their values of $(\psi_{\text{calc}}/\psi_{\text{obs}})$ are given in the last column of table 6. These values are more reasonable and are close to the experimental values.

4.3 Application to zinc blende and diamond structure crystals

Szigeti [3] obtained a value of 0.98 for $(\psi_{\text{calc}}/\psi_{\text{obs}})$ for ZnS; this is close to the values for the alkali halides. Szigeti [3] mentioned that the second relation is not applicable to non-centrosymmetric crystals like ZnS and he disposed off the value of 0.98 as probably due to errors in the experimental value of ψ_{obs} . However, Mitra and Marshall [31] repeated the calculation for ZnS using new experimental data but obtained a value of 1.08 for $(\psi_{\text{calc}}/\psi_{\text{obs}})$ which is close to Szigeti's value. Mitra and Marshall [31] also made calculations for several other crystals with ZnS structure (table 7) and obtained values of $(\psi_{\text{calc}}/\psi_{\text{obs}})$ close to unity like in the case of the alkali halides. It may be noted that these crystals are partially ionic (or partially covalent). More importantly, Mitra and Marshall [31] also applied eq. (46) to the fully covalent crystals with diamond structure. The values of $(\psi_{\text{calc}}/\psi_{\text{obs}})$ for these crystals (included in table 7) are also of the same order (~ 1). Thus, although Szigeti [3] has stated that eq. (46) may not be applicable to crystals like ZnS, the results of Mitra and Marshall show that, empirically at least, Szigeti's second relation (eq. (46)) is applicable to several crystals other than the alkali halides irrespective of the nature of bonding.

4.4 Application to alkaline earth oxides

Szigeti [3] applied eq. (46) to the alkaline earth oxides. His results are given in table 8. The $(\psi_{\text{calc}}/\psi_{\text{obs}})$ value for MgO is 0.47 which is much lower than the values for the highly ionic alkali halides. For CaO, the value is 0.13 which is even lower. For SrO, Szigeti [3] gave only the ψ_{calc} value as the experimental value was not known. The alkaline earth oxides are considered to be less ionic than the alkali halides [71]. The s values given in table 3 also indicate the same. But, in view of the discussion in §4.3, this should not have caused such a marked deviation of the $(\psi_{\text{calc}}/\psi_{\text{obs}})$ values from unity.

Szigeti's value of ψ_{calc} for MgO was based on an old value of ν_t [9]. Anderson and Glynn [68] redetermined ν_t from i.r. reflectivity curves and recalculated ψ_{calc} . Their value is given in table 8. With this value of ν_t , a value of 1.03 is obtained for $(\psi_{\text{calc}}/\psi_{\text{obs}})$ which is satisfactory. Regarding CaO, Szigeti had expressed a doubt about the reliability of the ψ_{obs} value used by him. Sirdeshmukh and Subhadra [72] used a new value of ψ_{obs} (table 8) and obtained a value of 0.67 for $(\psi_{\text{calc}}/\psi_{\text{obs}})$ which is of the right order. For SrO, using the compressibility data from Son and Bartels [70], Sirdeshmukh and Subhadra [72] obtained a value of 1.28 for $(\psi_{\text{calc}}/\psi_{\text{obs}})$ which, again, is of the right order.

The cases of MgO and CaO reveal a new application of Szigeti's second relation: when ν_t values and ψ_{obs} values are in doubt, Szigeti's relation can be used to sift out the correct value.

Table 7. Values of $(\psi_{\text{calc}}/\psi_{\text{obs}})$ for some crystals with zinc blende and diamond structures.

ZnS structure	$(\psi_{\text{calc}}/\psi_{\text{obs}})^{\text{a}}$	Diamond structure	$(\psi_{\text{calc}}/\psi_{\text{obs}})^{\text{a}}$
ZnS	(0.98)	C (diamond)	1.00
	1.09	Si	0.99
CdTe	1.14	Ge	0.88
GaAs	0.89		
GaSb	0.88		
InAs	0.91		
InSb	0.91		
AlSb	0.96		

^aValue in parenthesis from Szigeti [3] and the rest of the values from Mitra and Marshall [31].

Table 8. $(\psi_{\text{calc}}/\psi_{\text{obs}})$ values for alkaline earth oxides.

Crystal	$(10^{-12} \frac{\psi_{\text{calc}}}{\text{cm}^2 \text{ dyne}^{-1}})$	$(10^{-12} \frac{\psi_{\text{obs}}}{\text{cm}^2 \text{ dyne}^{-1}})$	$(\psi_{\text{calc}}/\psi_{\text{obs}})$
MgO	0.28 ^a	0.59 ^a	0.47
	0.61 ^b		1.03
CaO	0.60 ^a	4.57 ^a	0.13
	0.61 ^b	0.89 ^c	0.67
SrO	1.46 ^a	1.14 ^d	1.28

^aSzigeti [3]; ^bAnderson and Glynn [68]; ^cPerez-Albuerne and Drickamer [69]; ^dSon and Bartels [70].

5. Application of Szigeti's theory to the fluorite lattice

5.1 Effective ionic charge

Crystals with the fluorite structure are triatomic and cubic. Their properties indicate that they are essentially ionic. Szigeti [2] calculated the effective ionic charge s for the alkaline earth fluorides using eq. (10). In these calculations, he defined the reduced mass μ for this system as

$$(1/\mu) = (1/m_1) + (1/2m_2), \quad (51)$$

where m_1 is the mass of ion with higher valency and m_2 is the mass of the ion with lesser valency. The values of s obtained by Szigeti [2] for three CaF_2 -type crystals are given in table 9. These values of s are of the same order as, but systematically lower than, those for the highly ionic alkali halides.

The long-wave lattice dynamics of the fluorite lattice was studied by Axe [73]. For s he obtained the same relation (eq. (10)) as obtained by Szigeti [3] except that the definition of the reduced mass used by Axe [73] is

Table 9. Effective ionic charge s , anharmonic correction $G/(\varepsilon_s - \varepsilon_\infty)$ and compressibility ratio $(\psi_{\text{calc}}/\psi_{\text{obs}})$ for some crystals with fluorite structure.

Crystal	s		$G/(\varepsilon_s - \varepsilon_\infty)$		$(\psi_{\text{calc}}/\psi_{\text{obs}})$
	a	b	c	d	b
CaF ₂	0.74	0.83	0.040	0.046	1.10
SrF ₂	0.65	0.87	0.032	0.035	1.07
BaF ₂	0.70	0.89	0.036	0.033	1.18
CdF ₂		0.79		0.077	
PbF ₂		0.87	-0.197	-0.225 (RT) 0.46 (400 K)	
EuF ₂		0.83		0.026	
ThO ₂		0.61			
UO ₂		0.58			1.01

a: Szigeti [3]; b: CaF₂, SrF₂, BaF₂ [73]; CdF₂, PbF₂ [74]; ThO₂, UO₂ [75]; EuF₂ [76]; c: Samara [40]; d: Sirdeshmukh and Reddy [77].

$$(1/\mu) = (1/m_1) + (2/m_2). \quad (52)$$

The values of s obtained by Axe and his coworkers for several crystals with CaF₂ structure are given in table 9. The values for the fluorides are systematically larger than those obtained by Szigeti [3] and are closer to the alkali halide values. The s values for two oxides with CaF₂ structure are distinctly low and indicate ‘increased covalency’ [75].

5.2 Anharmonic correction

The anharmonic correction $G/(\varepsilon_s - \varepsilon_\infty)$ to s introduced by Szigeti [5] has been discussed earlier (eq. (17)). This correction has been worked out for some fluorite-type crystals by Samara [40] and by Sirdeshmukh and Reddy [77]. Their values are given in table 9. An interesting thing to note is that the correction $G/(\varepsilon_s - \varepsilon_\infty)$ is positive for all the crystals except PbF₂. More interesting is the observation of Sirdeshmukh and Reddy [77] that the correction for PbF₂ changes sign; negative at low temperatures and positive at elevated temperatures.

5.3 Modification of Szigeti’s second relation

Axe [75] also obtained a modified relation for the compressibility ψ in terms of the dielectric constant. This relation is

$$\psi^{-1} = (12r)^{-1} \{ 2[(\varepsilon_s + 2)/(\varepsilon_\infty + 2)]\mu(2\pi\nu_t)^2 + \mu_R(2\pi\nu_R)^2 \}. \quad (53)$$

Here, ν_R is the Raman mode frequency and μ_R is the mass of the fluorine (or oxygen ion). The main difference between this relation and Szigeti’s relation (eq. (46)) is the term in ν_R . The values of $(\psi_{\text{calc}}/\psi_{\text{obs}})$ where ψ_{calc} is the value calculated from eq. (53) are given in table 9. These are close to unity showing good agreement.

Table 10. Experimental values of γ_t and γ_R .

Crystal	γ_t			γ_R		
	Ferraro <i>et al</i> [79]	Lowndes [80]	Andeen <i>et al</i> [81]	Ferraro <i>et al</i> [79]	Ruppin [82]	Kessler <i>et al</i> [83]
CaF ₂	1.8	3.2	2.85	1.9	1.83	1.85
SrF ₂	1.2	3.1	2.61	–	–	1.60
BaF ₂	0.8	2.4	2.61	1.8	2.03	2.00

5.4 Raman mode Gruneisen parameter and strain derivative of effective ionic charge

By differentiation of Axe's second relation (eq. (53)), Sirdeshmukh *et al* [78] obtained the following relation for the Raman mode Gruneisen constant γ_R in terms of the transverse optic mode Gruneisen parameter γ_t :

$$\gamma_R = -(2r/\mu_R\psi\omega_R)[1 + (3/\psi^2)(\partial\psi/\partial P)_T] - (\mu/\mu_R)(\omega_t/\omega_R)^2[(\varepsilon_s + 2)/(\varepsilon_\infty + 2)](1/\psi). \quad (54)$$

Here, ω_R and ω_t are the Raman and transverse optic mode frequencies and γ_R and γ_t are the corresponding mode Gruneisen parameters $-(d \log \omega_R/d \log V)$ and $-(d \log \omega_t/d \log V)$ respectively. Equation (54) can be used to calculate γ_R with γ_t as input or vice versa. The experimental data on γ_R and γ_t are given in table 10. It can be seen that there is a large difference (of about 100–200 per cent) between the γ_t values reported by Ferraro *et al* [79] on the one hand and Lowndes [80] and Andeen [81] on the other. However, there is good consistency among the values of γ_R reported by Kessler *et al* [83] and other workers.

The values of γ_R calculated from eq. (54) using different γ_t values as input are given in table 11 and compared with the experimental values. It can be seen that only the γ_t values from Ferraro *et al* [81] yield γ_R values which compare well with the experimental γ_R values. γ_t values from other sources yield γ_R values that are either too small or even negative. Thus, eq. (54) is useful in sifting the correct γ_t value from a set of differing values.

By differentiation of Axe's first relation [75], which is the same as Szigeti's first relation, we get the strain derivative of the Szigeti charge:

$$(V/s)(ds/dV) = -(1/2\psi) \left[\frac{1}{(\varepsilon_s - \varepsilon_\infty)} \left\{ \left(\frac{\partial \varepsilon_s}{\partial P} \right) - \left(\frac{\partial \varepsilon_\infty}{\partial P} \right) \right\} - \left(\frac{2}{\varepsilon_\infty + 2} \right) \left(\frac{\partial \varepsilon_\infty}{\partial P} \right) (1 + 2\gamma_t) \right]. \quad (55)$$

This in essence is the same as eq. (43) except that the volume derivatives have been expressed as pressure derivatives. The values of $(V/s)(ds/dV)$ calculated from eq. (55) using as input the best value of γ_t are given in table 11. These values are of the same order as those for the alkali halides (table 4).

Table 11. Values of γ_t and γ_R and $(V/s)(ds/dV)$.

Crystal	γ_t	γ_R		$(V/s) (ds/dV)$
		Calc. (eq. (54))	Expt. (Kessler <i>et al</i> [85])	Calc. (eq. (55))
CaF ₂	1.8	1.41	1.85	0.86
	3.2	-0.65		
	2.85	0.16		
SrF ₂	1.2	3.1	1.6	1.42
	3.1	-0.94		
	2.61	-0.05		
BaF ₂	0.8	2.4	2.0	1.82
	2.4	0.03		
	2.61	-0.48		

6. Summary

Szigeti's [2,3] theory is by far the most comprehensive theory of dielectrics. It is applicable to diatomic as well as polyatomic crystals and to ionic as well as covalent crystals. Though the original theory assumed a harmonic crystal, Szigeti [4,5] modified it to make it applicable to an anharmonic crystal. The most important contribution of Szigeti's theory is the concept of the effective ionic charge; it has found several applications, the most important being its utility as an ionicity parameter. Several theoretical models have been proposed to account for the deviation of the effective ionic charge from unity. These models have provided an insight into the complex polarization mechanisms in solids. Some new applications and results have been discussed. These are: (i) Szigeti's second relation, relating the compressibility to the absorption frequency, has been found to be useful as a consistency check on compressibility data. (ii) Axe's modification [75] of Szigeti's theory has led to a method to estimate the mode Gruneisen parameter of fluorite-type crystals. (iii) Systematic calculation of the anharmonic correction for the alkali halides with NaCl structure has revealed that only LiBr has a negative correction. (iv) Two equations for the effective ionic charge by Havinga have been systematically applied to a number of alkali halides.

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