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Dielectric behaviour and optic mode Gruneisen parameters of the halides of silver, caesium and thallium

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Abstract. The optic mode Gruneisen parameters in silver, caesium and thallium halides are calculated using the Born model for interionic forces and the Szigeti theory of dielectric constants. The strain derivatives of the electronic and static dielectric constants are also evaluated and compared with experimental data. The strain derivative of static dielectric constant reveals the inadequacy of the Born model for the crystals under study. Possible modifications have been suggested to improve the situation. The theoretical values of the optic mode Gruneisen parameters closely agree with recent experimental data. An appropriate process has been adopted to evaluate the average values for the Gruneisen parameter.

Keywords. Gruneisen parameter; dielectric constants; Born model; Szigeti relations; silver halides; caesium halides; thallium halides.

1. Introduction

Studies on the Gruneisen parameters provide valuable information about the volume dependence of the frequency spectrum which is related to the thermodynamic and thermoelastic behaviour (Ruppin and Roberts 1971) and dielectric behaviour of solids under the effect of pressure (Lowndes and Martin 1970; Madan 1971). In recent years it has been possible, with the help of improved techniques, to measure the variation of dielectric constant and frequencies of lattice vibrations under hydrostatic pressure. This makes it desirable to extend the existing theories to investigate the behaviour of crystals under the effect of pressure. Recently, Singh *et al* (1977) have shown that the Born model and Szigeti relations give an adequate description of the pressure variation of transverse optic mode frequency in the entire family of NaCl structure alkali halides. It will be interesting as well as useful to investigate the applicability of the approach in other ionic crystals which are more complicated as far as the nature of the chemical bond is concerned. In the present paper we perform calculations of the optic mode Gruneisen parameters and strain derivatives of dielectric constants for AgCl, AgBr, CsCl, CsBr, CsI, TlCl, TlBr and TlI crystals. The halides of Ag and Tl show a remarkably different behaviour from that of alkali halides in respect of chemical bond, dielectric properties and elastic properties (Lowndes and Martin 1969; Philips 1970; Loje and Schuele 1970). In the following sections we give the method of calculation of various quantities and compare the results with experimental data.

2. Strain derivatives of electronic polarizability and electronic dielectric constant

The strain derivatives of electronic polarizability in alkali halides have recently been calculated by Sharma *et al* (1976) following the energy level analysis performed by Ruffa (1963). It is evident from recent studies (Jai Shanker and Verma 1975; Jai Shanker and Agrawal 1976) that Ruffa's energy level analysis yields reasonable values of electronic polarizabilities of ions even in crystals other than alkali halides. It is therefore plausible to make use of this approach to evaluate the strain derivatives of electronic polarizabilities in the crystals under study. Following Sharma *et al* (1976) we can write

$$d\alpha_+/dr = -\,[2\alpha_{f+}\,E_{f+}{}^2]\,/\,(E_{f+}\;eV_M)^3 - (eV_M\,/\,r), \tag{1}$$

and

$$d\alpha_-/dr = \alpha_-/r_-\,[1-(r_+/\alpha_+)\,(d\alpha_+/dr)] \tag{2}$$

where r is the interionic separation, α_+ and α_- are the electronic polarizabilities and r_+ and r_- are the radii of cation and anion respectively. The expression for the strain derivative of electronic or high frequency dielectric constant ϵ_∞ can be obtained from the Lorentz-Lorenz relation

$$(\epsilon_\infty - 1)/(\epsilon_\infty + 2) = (4\pi/3V)\,\alpha_\infty, \tag{3}$$

which yields

$$V\,(d\epsilon_\infty/dV) = -\,[(\epsilon_\infty - 1)\,(\epsilon_\infty + 2)]/3(1-\lambda), \tag{4}$$

where λ, the strain polarizability parameter, is given by

$$\lambda = (V/\alpha_\infty)\,(d\alpha_\infty/dV). \tag{5}$$

The electronic polarizability α_∞ can be expressed as the sum of the polarizabilities of individual ions (Tessman *et al* 1953)

$$\alpha_\infty = \alpha_+ + \alpha_-. \tag{6}$$

Since $V = kr^3$ ($k = 2$ for NaCl structure and 1·54 for CsCl structure), we can write from (5) and (6)

$$\lambda = \frac{1}{3}\,\frac{r}{\alpha_\infty}\left(\frac{d\alpha_\infty}{dr}\right) = \frac{1}{3}\,\frac{r}{\alpha_\infty}\left(\frac{d\alpha_+}{dr} + \frac{d\alpha_-}{dr}\right). \tag{7}$$

Making use of (1), (2), (4) and (7) one can calculate $V(d\epsilon_\infty/dV)$. The relevant input data are listed in table 1. It will be pertinent to mention here that if the variation of polarizability with strain is not taken into account i.e. $\lambda = 0$, we find

$$V(d\epsilon_\infty/dV) = -[(\epsilon_\infty - 1)\,(\epsilon_\infty + 2)]/3. \tag{8}$$

Table 1. Input data for the calculation of $V(d\epsilon_\infty/dV)$

Crystal	r (10^{-8} cm)	ϵ_∞	α_{f+} (10^{-24} cm^3)	eV_M (eV)	E_{f+} (eV)	α_+ (10^{-24} cm^3)	α_- (10^{-24} cm^3)	r_+ (10^{-8} cm)	r_- (10^{-8} cm)
AgCl	2·772^c	3·92^g	1·72^i	9·09	54·23	2·48^l	2·87^l	1·10^l	1·67^l
AgBr	2·884^c	4·62^g	1·72^i	8·73	54·23	2·44^l	3·69^l	1·09^l	1·79^l
CsCl	3·571^d	2·63^g	2·42^i	7·11	49·53	3·015^q	3·063^q	1·90^p	1·65^p
CsBr	3·720^d	2·78^g	2·42^i	6·83	49·53	3·015^q	4·276^q	1·90^p	1·81^p
CsI	3·956^d	3·02^g	2·42^i	6·42	49·53	3·015^q	6·517^q	1·90^p	2·05^p
TlCl	3·33^c	4·76^g	3·50^c	7·63	50·13	4·86^l	2·67^l	1·70^l	1·63^l
TlBr	3·44^c	5·34^g	3·50^c	7·38	50·13	4·80^l	3·45^l	1·69^l	1·75^l
TlI	3·62^c	7·73^h	3·50^c	7·02	50·13	4·73^l	5·17^l	1·68^l	1·94^l

c Mayer (1933b); *d* Tosi (1964); *g* Lowndes and Martin (1969); *h* Tessman *et al* (1953); *i* Pauling (1927); *l* Jai Shanker *et al* (1976); *q* Pirenne Kartheuser (1964); *p* Sysio (1969).

Table 2. Values of $(d\alpha_+/dr)$, $(d\alpha_-/dr)$, λ and $V(d\epsilon^{\infty}/dV)$

Crystal	$(d\alpha_+/dr)$ (10^{-16} cm^2) equation (1)	$(d\alpha_-/dr)$ (10^{-16} cm^2) equation (2)	λ equations (6) and (7)	$V(d\epsilon_\infty/dV)$ Calculated equation (4)	Experimental values based on equation (9)
AgCl	−0·36	1·99	0·28	−4·14	−1·76
AgBr	−0·32	2·36	0·32	−5·45	−1·99
CsCl	−0·31	2·22	0·37	−1·58	−1·02
CsBr	−0·28	2·78	0·42	−1·64	−1·25
CsI	−0·24	3·64	0·47	−1·78	−1·66
TlCl	−0·52	1·94	0·21	−6·71	−5·20
TlBr	−0·48	2·31	0·25	−7·95	−6·79
TlI	−0·43	3·07	0·32	−14·82	—

Equation (8) was used by Burstein and Smith (1948a, 1948b) to study the photoelastic behaviour of crystals. The experimental values of $V(d\epsilon_\infty/dV)$ can be derived from the data on photoelastic constants. Unfortunately the photoelastic constants have not been measured for the crystals under study. Mueller (1935) has, however, suggested that in the absence of such data, one can make use of the temperature dependence of dielectric constant. Lowndes and Martin (1969) have reported the temperature dependence of ϵ_∞. These data can be reduced to yield the strain derivatives of ϵ_∞ using the relation

$$V(d\epsilon_\infty/dV) = (1/\beta)\,(d\epsilon_\infty/dT), \tag{9}$$

where β is the volume thermal expansion coefficient. A comparison of the calculated and experimental values is presented in table 2.

3. Strain derivatives of static polarizability and static dielectric constant

The static dielectric constant corresponds to the low frequency region where the polarization arising from the relative displacement of the ions also contributes to the polarizability. Following the Clausius-Mossotti relation one can express the static dielectric constant ϵ_0 as

$$(\epsilon_0-1)/(\epsilon_0+2) = (4\pi/3V)\alpha_0 \tag{10}$$

where α_0, the static polarizability, can be expressed as the sum of electronic and ionic polarizabilities

$$\alpha_0=\alpha_\infty+\alpha_i. \tag{11}$$

For α_i, which arises from the relative displacement of ions, one can write

$$\alpha_i = (Ze)^2/f \tag{12}$$

where Ze is the ionic charge and f the short range force constant.

Following expression for the strain derivative of ϵ_0 can be obtained from (10)

$$V(d\epsilon_0/dV) = -\,[(\epsilon_0 - 1)(\epsilon_0 + 2)]/3\,[1 - (V/\alpha_0)(d\alpha_0/dV)]. \tag{13}$$

From (11) we have

$$(d\alpha_0/dV) = (d\alpha_\infty/dV) + (d\alpha_i/dV). \tag{14}$$

The method for evaluating $(d\alpha_\infty/dV)$ has been given in the preceding section. For estimating $(d\alpha_i/dV)$ we use (12) which yields

$$(d\alpha_i/dV) = -\,(1/f)\,(df/dV)\alpha_i\,. \tag{15}$$

From the theory of ionic crystals (Born and Huang 1954), we have

$$f = (1/3)\,[\phi''(r) + (2/r)\,\phi'(r)], \tag{16}$$

so that

$$\frac{V}{f}\left(\frac{df}{dV}\right) = \frac{r[\phi'''(r)+(2/r)\phi''(r)-(2/r^2\phi'(r)]}{3[\phi''(r)+(2/r)\phi'(r)]} \tag{17}$$

where $\phi'(r)$, $\phi''(r)$ and $\phi'''(r)$ are the first, second and third order derivatives of the short range energy $\phi(r)$ with respect to r. The binding energy of an ionic crystal can be expressed as

$$W = -(e^2\delta/r) + \phi(r) \tag{18}$$

where δ is the Madelung constant and

$$\phi(r) = B(r) - (C/r^6) - (D/r^8). \tag{19}$$

$B(r)$ is the overlap repulsive energy, C and D are the van der Waals dipole-dipole and dipole-quadrupole coefficients. For $B(r)$, we adopt two potential functions, an inverse power law $B_1 r^{-n}$ and the exponential law $B_2 \exp(-r/\rho)$. The repulsive parameters B_1, B_2, n and ρ are derived from the Hildebrand equation of state (Tosi 1964). Values of C and D are taken from Mayer (1933a, 1933b). Values of f and (df/dV) calculated from (16) and (17) are given in table 3 along with the repulsive potential parameters. It may be pointed out here that the two potential functions lead to the same value for f as $n \equiv (r/\rho) - 1$. Using the values of f, $(V/f)\,(df/dV)$ and $(d\alpha_\infty/dV)$ and taking the values of ϵ_0 from Lowndes and Martin (1969) and Samara (1968) we have calculated α_0, $(d\alpha_0/dV)$ and $V(d\epsilon_0/dV)$ from (11)–(15). These are given in table 4 along with the experimental values.

4. Evaluation of the optic mode Gruneisen parameters

Szigeti (1949, 1950) derived the following relation for the transverse optic mode frequency ω_{TO}

$$\omega_{\mathrm{TO}}^2 = f(\epsilon_\infty + 2)/\mu(\epsilon_0 + 2), \tag{20}$$

Table 3. Values of the Born repulsive parameters, f and $(V/f)\,(df/dV)$

Crystal	Born repulsive parameters derived from								$f(10^4$ dynes/cm)		$(V/f)\,(df/dV)$			
	Elastic data				Dielectric data				Elastic data	Dielectric data	Elastic data		Dielectric data	
	n	$B_1 r^{-n}$ (ergs)	ρ (Å)	$B_2 \exp(-r/\rho)$ (ergs)	n	$B_1 r^{-n}$ (ergs)	ρ (Å)	$B_2 \exp(-r/\rho)$ (ergs)			Inverse Power Form	Exponential Form	Inverse Power Form	Exponential Form
AgCl	9·38	2·89	0·267	2·61	10·43	2·60	0·242	2·37	6·91	8·15	−4·20	−3·61	−4·62	−4·07
AgBr	9·49	2·78	0·275	2·52	11·30	2·34	0·234	2·14	6·29	8·21	−4·25	−3·67	−4·95	−4·43
CsCl	9·55	1·73	0·338	1·56	12·88	1·28	0·257	1·19	2·97	4·41	−4·10	−3·59	−5·31	−4·86
CsBr	9·72	1·68	0·347	1·52	13·77	1·19	0·252	1·11	2·74	4·33	−4·19	−3·67	−5·65	−5·21
CsI	9·80	1·60	0·366	1·45	15·11	1·04	0·245	0·97	2·33	4·11	−4·23	−3·72	−6·14	−5·70
TlCl	8·54	2·82	0·349	2·53	11·28	2·13	0·271	1·96	3·55	5·54	−3·89	−3·24	−4·99	−4·45
TlBr	8·60	2·77	0·358	2·48	10·97	2·17	0·287	1·98	3·28	4·87	−4·19	−3·28	−4·88	−4·34
TlI	8·56	2·77	0·378	2·48	14·08	1·69	0·240	1·57	2·86	6·20	−3·94	−3·27	−6·06	−5·57

Table 4. Values of α_0, $(d\alpha_0/dV)$ and $V(d\epsilon_0/dV)$

Crystal	$\alpha_0(10^{-24}\,\mathrm{cm}^3)$		$d\alpha_0/dV$					$V(d\epsilon_0/dV)$				
			Elastic data		Dielectric data		Experimental values calculated from eqs (10) & (13)	Elastic data		Dielectric data		Experimental
	Elastic data	Dielectric data	Inverse Power Form	Exponential Form	Inverse Power Form	Exponential Form		Inverse Power Form	Exponential Form	Inverse Power Form	Exponential Form	
AgCl	8·68	7·85	0·36	0·32	0·34	0·30	0·44	34·86	24·87	38·04	29·12	62·66^a
AgBr	9·79	9·07	0·36	0·32	0·33	0·30	0·43	43·39	31·22	41·29	32·27	70·57^a
CsCl	13·83	11·13	0·48	0·43	0·43	0·39	0·30	25·79	20·66	30·12	26·32	15·79^c
CsBr	15·72	12·37	0·48	0·43	0·42	0·39	0·30	23·46	18·92	27·43	24·29	14·74^c
CsI	19·41	14·77	0·49	0·43	0·41	0·38	0·27	21·87	17·77	25·77	23·13	11·36^c
TlCl	14·02	11·71	0·47	0·40	0·39	0·35	0·29	330·19	220·86	329·33	260·30	119·71^a
TlBr	15·27	13·58	0·50	0·40	0·40	0·36	0·29	332·76	200·99	271·68	210·12	113·06^a
TlI	17·95	15·78	0·48	0·40	0·35	0·33	0·27	282·27	191·60	189·51	154·66	74·51^b

a —Lowndes (1972) *b* —Samara (1968) *c* —Lowndes and Martin (1970)

Table 5. Values of ω_{TO}, γ_{TO}, γ_{LO}, $\bar{\gamma}$ and γ_G

Crystal	ω_{TO} (10^{13} s^{-1})			γ_{TO}					γ_{LO}				$\bar{\gamma}$				γ_G
				Elastic data		Dielectric data			Elastic Data		Dielectric data		Elastic data		Dielectric data		
	Elastic data	Dielectric data	Experimental[a]	Inverse Power Form	Exponential Form	Inverse Power Form	Exponential Form	Experimental[b]	Inverse Power Form	Exponential Form	Inverse Power Form	Exponential Form	Inverse Power Form	Exponential Form	Inverse Power Form	Exponen tial Form	
AgCl	2·65	2·88	1·99	4·63	4·34	4·84	4·57	4·34±0·16	1·60	1·30	1.80	1·53	2·39	2·09	2·59	2·32	1·97
AgBr	1·95	2·22	1·50	4·72	4·43	5·07	4·81	4·41±0·19	1·67	1·37	2·02	1·75	2·49	2·20	2·85	2·58	2·06
CsCl	1·82	2·21	1·87	3·04	2·79	3·65	3·42	3·14±0·10	1·71	1·46	2·32	2·09	2·08	1·82	2·68	2·46	2·14
CsBr	1·35	1·70	1·38	3·08	2·82	3·81	3·58	2·74±0·05	1·74	1·49	2·48	2·25	2·14	1·88	2·87	2·64	2·14
CsI	1·13	1·50	1·17	2·95	2·69	3·90	3·68	2·42±0·08	1·80	1·54	2·75	2·54	2·16	1·91	3·12	2·90	2·16
TlCl	1·18	1·47	1·19	4·06	3·73	4·61	4·34	3·62±0·20	1·68	1·35	2·22	1·96	1·98	1·66	2·53	2·26	—
TlBr	0·88	1·07	0·90	4·30	3·85	4·65	4·37	4·30±0·16	1·81	1·35	2·15	1·88	2·18	1·72	2·53	2·25	—
TlI	0·82	1·21	—	3·91	3·57	4·97	4·72	—	1·69	1·36	2·75	2·51	2·15	1·82	3·21	2·97	—

a —Lowndes and Martin (1969) b —Lowndes and Rastogi (1976) where μ is the reduced mass per ion pair. Using the values of f, ϵ_0 and ϵ_∞ one can evaluate ω_{TO} from (20). Values of ω_{TO} thus calculated present close agreement with experimental data (table 5).

The following expression for the transverse optic mode Gruneisen parameter γ_{TO} can be obtained from (20)

$$\gamma_{TO} = -\frac{V}{\omega_{TO}}\left(\frac{d\omega_{TO}}{dV}\right) = -\frac{1}{2}\left[\frac{V}{f}\left(\frac{df}{dV}\right) - \frac{V}{(\epsilon_0+2)}\left(\frac{d\epsilon_0}{dV}\right) + \frac{V}{(\epsilon_\infty+2)}\left(\frac{d\epsilon_\infty}{dV}\right)\right]. \tag{21}$$

From the LST (Lyddane *et al* 1941) relation we have

$$(\omega_{LO}/\omega_{TO})^2 = (\epsilon_0/\epsilon_\infty), \tag{22}$$

where ω_{LO} is the longitudinal optic mode frequency. Equation (22) yields

$$\gamma_{LO} = \gamma_{TO} - \tfrac{1}{2}\left[\frac{V}{\epsilon_0}\left(\frac{d\epsilon_0}{dV}\right) - \frac{V}{\epsilon_\infty}\left(\frac{d\epsilon_\infty}{dV}\right)\right]. \tag{23}$$

Values of γ_{TO} and γ_{LO} calculated from (21) and (23) are given in table 5 along with available experimental data. An average value of the Gruneisen parameter ($\bar{\gamma}$) can be obtained from the method suggested by Barron (1955, 1957) and adopted by Madan (1971). Following these investigators one can write

$$\bar{\gamma} = \frac{\gamma_{TO}\omega_{TO}^2 + \gamma_{LO}\,\omega_{LO}^2}{\omega_{TO}^2 + \omega_{LO}^2}. \tag{24}$$

Values of $\bar{\gamma}$ calculated from (24) are given in table 5. The Gruneisen parameter is an important and useful quantity related to the thermal and elastic properties of solids. Values of this parameter can also be derived from the thermoelastic data using the relation

$$\gamma_G = (\beta V/\chi_T C_v), \tag{25}$$

where χ_T is the isothermal compressibility and C_v the specific heat at constant volume. It is interesting to compare $\bar{\gamma}$ and γ_G obtained from (24) and (25) respectively (table 5).

5. Results and discussion

In the present study we have considered eight crystals of heavier metal halides with NaCl and CsCl structures. It is found that the values of the strain polarizability parameter λ are less than 1 and those of $V(d\epsilon_\infty/dV)$ are negative for all the crystals under study. This implies that the high frequency dielectric constant increases with pressure. In this respect the crystals under consideration are similar to NaCl structrue alkali halides (Sharma *et al* 1976). It should be noted that the experimental values of $V(d\epsilon_\infty/dV)$ are smaller than the calculated ones. This discrepancy is due to the fact that there is some purely temperature dependent contribution of the polarizability. The values quoted as experimental (table 2) are derived from the temperature dependence of ϵ_∞ using (9). In fact, the change in electronic polarizabilities of ions due to the change in temperature arises from (i) purely volume dependent contribution and (ii) purely temperature dependent contribution (Vedam *et al* 1975). Equation (9) holds strictly only if contribution (ii) is zero. A comparison of calculated values with those obtained from (9) reveals that the temperature dependence of electronic polarizability at constant volume is relatively larger in AgCl and AgBr than that in caesium and thallium halides.

It is observed from table 4 that α_0, $(d\alpha_0/dV)$ and $V(d\epsilon_0/dV)$ calculated in the present study show significant deviations from the experimental values. This suggests that the Born model analysis is not adequate for the crystals under study. It is pertinent to mention here that the strain dependence of ϵ_∞ and ϵ_0 for Cs halides were first calculated by Srinivasan and Srinivasan (1973) using an ion polarizable shell model. These investigators used an exponential form of the Born repulsive energy and found that the calculated $(1/\epsilon_0)(d\epsilon_0/dP)$ were about 70 to 100% more than the measured values. This result agrees with our predictions for CsCl, CsBr and CsI (table 4). It should be emphasized that in calculating the values of α_i and $(d\alpha_i/dV)$ the charge on the ions has been considered to be Ze with $Z = 1$ and e the electronic charge. In fact the classical theory cannot explain the dielectric behaviour of ionic crystals unless the effective charge parameter is introduced for ions (Szigeti 1949, 1950). If Z^*e be the effective ionic charge, (12) will be modified to

$$\alpha_i = (Z^*e)^2/f. \tag{26}$$

Values of Z^* which will yield α_i and α_0 in agreement with experiment are listed in table 6 and compared with the effective charge parameter calculated by Lowndes and Martin (1969) using experimental data on ϵ_0, ϵ_∞ and ω_{TO} and making use of the Szigeti relation

$$\epsilon_0 - \epsilon_\infty = [4\pi(Z^*e)^2/9V]\ [(\epsilon_\infty + 2)^2/\mu\omega_{\mathrm{TO}}^2]. \tag{27}$$

Equation (26) leads to the following expression

$$\frac{d\alpha_i}{dV} = 2\frac{\alpha_i}{Z^*}\left(\frac{dZ^*}{dV}\right) - \frac{\alpha_i}{f}\left(\frac{df}{dV}\right). \tag{28}$$

Values of (dZ^*/dV) which produce $(d\alpha_i/dV)$ or $(d\alpha_0/dV)$ in agreement with experiment, are given in table 6. One can also evaluate (dZ^*/dV) by taking the volume derivative of (27) which yields

$$\frac{V}{Z^*}\left(\frac{dZ^*}{dV}\right) = \tfrac{1}{2} - \gamma_{\mathrm{TO}} - \left[\frac{1}{(\epsilon_\infty+2)} + \frac{1}{2(\epsilon_0-\epsilon_\infty)}\right] V\left(\frac{d\epsilon_\infty}{dV}\right)$$
$$+\frac{V}{2(\epsilon_0-\epsilon_\infty)}\left(\frac{d\epsilon_0}{dV}\right). \tag{29}$$

Table 6. Values of Z^* and (V/Z^*) (dZ^*/dV)

Crystal	Z^* Calculated equations (12) and (26)	Z^* Experimental (Lowndes and Martin 1969)	(V/Z^*) $[(dZ^*)/(dV)]$ Inverse Power equation (28)	(V/Z^*) $[(dZ^*)/(dV)]$ Exponential power Form equation (28)	(V/Z^*) $[(dZ^*)/(dV)]$ Experimental based on equation (29)
AgCl	0·92	0·69	0·62	0·92	0·90
AgBr	0·88	0·68	0·73	1·02	1·04
CsCl	0·82	0·85	−0·37	−0·11	−0·47
CsBr	0·80	0·82	−0·25	0·01	0·08
CsI	0·75	0·78	−0·27	−0·02	0·25
TlCl	0·80	0·87	−0·31	0·02	−0·09
TlBr	0·82	0·86	−0·47	−0·02	−0·44

A comparison of (V/Z^*) (dZ^*/dV) obtained from (28) and (29) is presented in table 6. Values of ω_{TO} and γ_{TO} reported in table 5 present good agreement with recent experimental data. Value of γ_{LO} is smaller than γ_{TO} for the crystals under study. It is interesting to mention here that the optic mode Gruneisen parameters of TlBr were calculated by Srinivasan *et al* (1975) using a variable charge shell model. Their values for γ_{TO} and γ_{LO} are respectively 4·05 and 1·05 and in good agreement with our results.

An alternative explanation of the discrepancy between calculated and experimental α_t can also be provided without introducing the concept of the effective charge parameter. This can be done by deriving the Born repulsive parameters from the values of α_t corresponding to the experimental data of static dielectric constant as suggestep by Boswarva and Simpson (1973). The parameters thus obtained are given in table 3. These differ significantly from the corresponding parameters derived from the compressibility data (table 3). It has been argued by Boswarva and Simpson that for studying the dielectric behaviour of ionic crystals one should make use of the short range parameters based on dielectric data. In view of this argument the calculations for $(d\alpha_0/dV)$, $V(d\epsilon_0/dV)$, ω_{TO}, γ_{TO}, γ_{LO} and $\bar{\gamma}$ have been repeated using the dielectric parameters. The results have been included in tables 4 and 5. We observe from there that the use of dielectric parameters does not improve the agreement between the experimental and calculated values of $V(d\epsilon_0/dV)$ and γ_{TO}. It is therefore evident that the dielectric behaviour of the crystals under study is better explained by introducing the concept of effective charge parameter in the theory of dielectric polarization.

6. Conclusions

We have thus presented an analysis of the strain dependence of dielectric constants and optic mode frequencies of the halides of silver, caesium and thallium using the Born model and the Szigeti relations. The calculated values of $V(d\epsilon_\infty/dV)$ and γ_{TO} are found to be consistent with experimental data. It has been demonstrated that consideration of the effective charge parameter and its volume dependence is essential to explain the static polarizability and its variation under hydrostatic pressure.

For AgCl and AgBr, the temperature dependence of the electronic polarizability and volume dependence of the effective charge parameter are significantly larger than those for the halides of caesium and thallium.

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