

ing field. The strength of polarisation increased with impressing stress resulting in a higher net polarization at the surface of the sample.

The stress dependence of the generated charges is linear because the charges appearing on the electrode surfaces maintain an electric field in the same direction as the original poling field. This field encourage the domains to be reoriented after releasing the static stress.

The non-linear behaviour of the stress dependence of the electric field is due to piezoelectrically generated electric field tend to maintain in the opposite direction to the original poling field and domain reorientation occurs even less readily under open circuit than short circuit conditions. It is obvious that the behaviour of the piezoelectric effect in polarized sod. ben. ac. is similar to that of the sod. acetylacetonate. The increase of conduction through the sample with raising temperature (figure 3) caused the decrease of the piezoelectric response due to disturbance of the dipole orientation.

At 70°C the polarisation disappeared and the material became unpiezoelectric due to partial chemical transformation that took place in the material.

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Analysis of the strain derivative of the Szigeti effective charge parameter in alkali halides

JAI SHANKER, V. P. GUPTA* AND O. P. SHARMA

Department of Physics, Agra College, Agra-282002

(Received 25 July 1977)

The concept of effective ionic charge introduced by Szigeti (1949, 1950) has been widely used in the studies of dielectric and lattice dynamical behaviour of ionic crystals. An excellent discussion of the Szigeti effective charge parameter e_s^* for alkali halides has been made by Lowndes & Martin (1969). Studies based on the various theoretical models (Dick & Overhauser 1958, Hardy 1962, Mitskevitch 1964) have revealed that the deviation of e_s^* from the nominal charge can be interpreted as a measure of ionic distortions in crystals. The amount of overlap and

* Department of Physics, Govt. P.G. College, Morena, M.P.

distortion of ions in crystals under the effect of pressure should increase as the volume is decreased. This expectation should lead to the positive values of $\frac{de_s^*}{dv}$. However, the predictions made by Jones (1967) and Barron & Batana (1969) are not consistent with this criterion. These investigators have obtained negative values of $\frac{de_s^*}{dv}$ for alkali halides leading to the conclusion that ionic distortion decreases when the crystal is compressed. This anomaly has also been discussed by Fontanella *et al* (1972) and Hardy & Karo (1973) leaving the question unanswered. In particular, it should be mentioned that Hardy & Karo (1973) have used an expression for the strain derivative of high frequency dielectric constant (eq. 3.21 in their paper) which is not in agreement with experimental data on photoelasticity (Sharma *et al* 1976).

According to Szigeti (1950) we have the relation

$$\epsilon_0 - \epsilon_\infty = \frac{4\pi}{9V} \frac{(\epsilon_\infty + 2)^2 e_s^{*2}}{\mu \omega^2 \tau_0} \tag{1}$$

where ϵ_0 and ϵ_∞ are the low frequency (static) and high frequency (electronic) dielectric constants respectively. μ is the reduced mass per ion pair, $\omega\tau_0$ the transverse optic mode frequency and V the volume per ion pair. Differentiation of eq. (1) with respect to volume yields

$$\begin{aligned} \frac{V}{e_s^*} \left(\frac{de_s^*}{dV} \right) &= 0.5 - \gamma_{T_0} - \left[\frac{1}{(\epsilon_\infty + 2)} + \frac{1}{2(\epsilon_0 - \epsilon_\infty)} \right] V \left(\frac{d\epsilon_\infty}{dV} \right) \\ &+ \frac{1}{2(\epsilon_0 - \epsilon_\infty)} V \left(\frac{d\epsilon_0}{dV} \right) \end{aligned} \tag{2}$$

where γ_{T_0} , the transverse optic mode Gruneisen parameter is given by

$$\gamma_{T_0} = - \frac{V}{\omega\tau_0} \left(\frac{d\omega\tau_0}{dV} \right) \tag{3}$$

Expressions identical to eq (2) have been used by Jones (1967), Barron & Batana (1969) and Fontanella *et al* (1972) to estimate the values of $\frac{V}{e_s^*} \left(\frac{de_s^*}{dV} \right)$. However, the experimental data used by these investigators were not good particularly for γ_{T_0} (having an uncertainty of about 30%). Very recently Lowndes & Rastogi (1976) have measured γ_{T_0} for many alkali halides, which are quite accurate and can be used with confidence to derive $\left(\frac{de_s^*}{dV} \right)$ from eq (2) which may lead to some decisive conclusion. We have evaluated $\frac{V}{e_s^*} \left(\frac{de_s^*}{dV} \right)$ from eq. (2) for 10 alkali halides with NaCl structure. These are listed in table-1 alongwith the input

data We have been careful in selecting the most recent and reliable experimental data on the dielectric constants and their strain derivatives (table 1). Values of $\frac{V}{e_s^*} \left(\frac{de_s^*}{dV} \right)$ obtained from the recent data used in the present study differ appreciably from those estimated by Jones (1967) and by Barron & Batana (1969).

It is remarkable to note from table-1 that $\frac{V}{e_s^*} \left(\frac{de_s^*}{dV} \right)$ are positive for all the crystals under consideration. This implies that the overlap and distortion of ions increase when the crystal is compressed, a physically plausible prediction. The anomaly observed by Barron & Batana (1969) and further discussed by Fontanella *et al* (1972) thus seems to be removed

Barron and Batana have suggested a theoretical method based on the deformation dipole model (DDM) of Hardy (1960) and Mitskevitch (1964) Following DDM one can express the deviation of the effective charge from its nominal value as

$$e_s^* - e = 2m'(r) - 4m(r)/r \quad \dots (4)$$

Table 1

Crystal	γ_{T_0}	ϵ_0	ϵ_∞	$V \left(\frac{de_\infty}{dV} \right)$	$V \left(\frac{de_0}{dV} \right)$	$\frac{V}{e_s^*} \left(\frac{de_s^*}{dV} \right)$	Deformation Dipole model (eq. 6)
	Lowndes and Rastogi (1976)	Lowndes and Martin (1969)	Lowndes and Martin (1969)				
LiF	2.35	8.50	1.93	-0.37 ^a	30.00 ^b	0.55	0.56
NaF	2.08	4.73	1.75	-0.33 ^b	12.70 ^b	0.69	0.50
NaCl	2.50	5.45	2.35	-0.74 ^a	11.50 ^b	0.62	0.96
NaBr	2.37	5.78	2.64	-0.99 ^b	15.90 ^b	1.03	1.07
KCl	2.28	4.49	2.20	-0.68 ^a	9.11 ^b	0.52	0.82
KBr	2.06	4.52	2.39	-1.08 ^a	8.92 ^b	1.04	1.09
KI	2.20	4.68	2.68	-1.40 ^a	6.58 ^a	0.58	1.29
RbCl	2.16	4.53	2.20	-1.01 ^c	8.22 ^d	0.57	0.81
RbBr	2.39	4.51	2.36	-1.24 ^c	7.37 ^a	0.40	0.96
RbI	2.09	4.55	2.61	-1.41 ^c	6.39 ^a	0.73	1.27

- (a) Van Vochten J. A. 1969 *Phys. Rev.* **182**, 891
- (b) Fontanella J. Andeen C. & Schuele D. 1972 *Phys. Rev.* **B6**, 582.
- (c) Srinivasan R. & Srinivasan K. 1973 *Phys. Stat. Sol.* (b) **57**, 757.
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where $m(r)$ is the deformation dipole moment due to an ion pair and $m'(r)$ is its derivative with respect to ionic separation r . It has been suggested (Lowndes & Martin 1970) that $m(r)$ varies exponentially with r

$$m(r) = m_0 \exp(-r/\rho) \quad \dots (5)$$

where ρ is the Born repulsive hardness parameter. Eqs (4) and (5) gives

$$\frac{V}{e_s^*} \left(\frac{de_s^*}{dV} \right) = \frac{1}{3} \left[\frac{r}{\rho} - \frac{2\rho}{(r-2\rho)} \right] \left(\frac{e}{e_s^*} - 1 \right) \quad (6)$$

Values of $\frac{V}{e_s^*} \left(\frac{de_s^*}{dV} \right)$ calculated from eq. (6) are compared in table 1 with the corresponding values derived from the experimental data.

Finally, it should be mentioned that Lawaetz (1971) has investigated a relationship between e_s^* and the Phillips electronegativity parameter C

$$e_s^* \simeq \frac{C}{\hbar\omega_p} \quad \dots (7)$$

where $\hbar\omega_p$ is known as the plasma energy and varies as $V^{-0.5}$. Volume derivative of eq (7) yields

$$\frac{V}{e_s^*} \left(\frac{de_s^*}{dV} \right) \simeq \frac{V}{C} \left(\frac{dC}{dV} \right) + 0.5 \quad \dots (8)$$

Van Vechten (1969) has discussed at length that for highly ionic solids like alkali halides $\frac{V}{C} \left(\frac{dC}{dV} \right) \simeq 0$ and hence $\frac{V}{e_s^*} \left(\frac{de_s^*}{dV} \right) \simeq 0.5$. It can be seen from table 1 that this prediction holds well for most of the crystals under study.

Financial assistance received from the UGC, India is gratefully acknowledged. Thanks are due to Professor M. P. Verma, Head of Physics Department Agra College Agra for providing the facilities.

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