MASTER

C00-623-165

SOLID STATE PHYSICS PROGRAM

THE DIELECTRIC PROPERTIES OF SOME ALKALI HALIDES

JOHN JOSEPH FONTANELLA

ATOMIC ENERGY COMMISSION

TECHNICAL REPORT NO. 69

CONTRACT NO. AT (11-1)-623

JANUARY, 1971

CASE WESTERN RESERVE UNIVERSITY

UNIVERSITY CIRCLE

CLEVELAND, OHIO 44106

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

The Dielectric Properties of Some Alkali Halides

Abstract

by

JOHN JOSEPH FONTANELLA

The room temperature static dielectric constants and their pressure and temperature derivatives for LiF, NaF, NaCl, NaBr, KCl, and KBr are reported. The static dielectric constants are measured to an accuracy of 0.01% by the method of substitution. The results are used to discuss the validity of the various microscopic models of the static dielectric constant of ionic crystals.

First, second, and third order pressure derivatives are measured to an estimated accuracy of 0.2%, 2%, and 20%, and first and second order temperature derivatives are determined with uncertainties on the order of 0.3% and 30% using highly refined capacitance techniques. The results are discussed in terms of the temperature independent volume derivative of the Szigeti effective charge and the volume independent temperature derivative of the static dielectric constant.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS

	<u>Page No.</u>
ABSTRACT	ii
ACKNOWLEDGEMENTS	iii
TABLE OF CONTENTS	iv
LIST OF FIGURES	vi
LIST OF TABLES	ix
INTRODUCTION	1
THEORY	3
A. The Static Dielectric Constant of Ionic Crystals	3
B. The Pressure and Temperature Derivatives of the SDC.	15
1. The Volume Dependent Effect	21
2. The Volume Independent Effect	24
EXPERIMENTAL PROCEDURE	29
A. The Static Dielectric Constant	29
B. The Pressure and Temperature Derivatives of the SDC	29
1. Samples	29
2. Pressure Derivatives	29
3. Temperature Derivatives	30
RESULTS	35
A. The Static Dielectric Constant	35
B. The Pressure Derivatives of the SDC	35
1. Raw Data	35
2. Data Reduction	40
C. The Temperature Derivatives of the SDC	47
1. Raw Data	47
2. Data Reduction	50

	<u>Page No.</u>
DISCUSSION	53
A. The Static Dielectric Constant	53
B. The Pressure and Temperature Derivatives of the SDC	65
1. The Volume Dependent Effect	72
2. The Volume Independent Effect	79
CONCLUSIONS	84
REFERENCES	85
APPENDIX	
I. Literature on Dielectric Formalism Applicable to Ionic Crystals Since 1950 Referred to in the Text but not Specifically Cited.	89
II. Relations of the Temperature and Pressure Derivatives of the Static Dielectric Constant to Experimental Observables.	93
III. Derivation of the Second Order Volumetric Derivatives of the SDC.	95

LIST OF FIGURES

<u>Figure No.</u>		<u>Page No.</u>
1.	Block diagram of the apparatus used for the measurement of the room temperature (308°K) pressure derivatives of the SDC.	31
2.	Maraging steel bomb and associated parts: a) BNC connectors; b) Maraging steel collar; c) O-Ring; d) Beryllium copper armor ring; e) Aluminum jacket; f) High pressure electrical lead through; g) Sample; i) Brass can; j) Glass-encapsulated thermistor; k) Heating resistor; l) Maraging steel closure plug.	32
3.	Block diagram of the apparatus used for the measurement of the zero pressure temperature derivatives of the SDC.	33
4.	Plot of pressure versus capacitance change for the alkali halides.	36

LIST OF TABLES

<u>Table</u>		<u>Page No.</u>
1.	Room temperature (300°K) basic data and the results of its application to the simple Born model compared to an average of the experimental results of this work.	10
2.	Pressure and temperature variation of optical and infrared properties of ionic crystals.	22
3.	Coefficients in the equation: $C/C_0 = 1 - A_1p + A_2p^2 - A_3p^3$ where p is in units of dynes/cm ² .	37
4.	Zero pressure logarithmic pressure derivatives of the capacitance of the chosen alkali halide.	41
5.	Basic data used in the reduction of room temperature (308°K) pressure and temperature derivatives.	42
6.	Pressure Derivatives of the SDC of Some Alkali Halides.	45
7.	Literature Values of the Pressure Derivatives of the SDC.	46
8.	The Coefficients in the Equation $C/C_0 = 1 + B_1(T-T_0) + B_2(T-T_0)^2$ and the Related Temperature Derivatives of the Capacitance.	49
9.	Temperature Derivatives of the Dielectric Constants of Some Alkali Halides.	51
10.	Literature Values of the Temperature Derivatives of the SDC.	52
11.	Various aspects of the polarizability of the alkali halides being investigated.	54

<u>Table</u>		<u>Page No.</u>
12.	Considerations Related to the Effective Charge.	57
13.	Quantum Theoretical Calculation of ϵ_s , n^2 and e^*/e for LiF.	64
14.	0°K Basic Data and the Szigeti Effective Charge.	66
15.	Pressure and Temperature Derivatives of the Polarizability.	67
16.	Contributions to the First Pressure Derivatives of the Total and Electronic Dielectric Constants.	68
17.	Contributions to the Experimental First Temperature Derivative of the SDC and to the quantity $1/\alpha(\partial\alpha/\partial T)_p$.	70
18.	Various Thermodynamic Derivatives of the Polarizability of Some Alkali Halides.	71
19.	First Order Volume Derivatives of the SDC of Some Alkali Halides.	73
20.	Calculations Related to the Volume Variation of the Szigeti Effective Charge and Longitudinal Optical Gruneisen Parameters.	75
21.	Second Order Volume Derivatives of the SDC of Some Alkali Halides.	78
22.	Thermodynamic Separation of the Temperature Derivatives of the SDC.	80
23.	The Anharmonic Contribution to the Lattice Dielectric Constant.	82

INTRODUCTION

The static dielectric constant (hereafter referred to as SDC) and its variation with pressure and temperature contain important information toward answering the question, Why is a solid? The constant itself is a direct measure of the ability of electron-nucleus, ion-ion, "free" electron, or polar configurations within a solid to respond to an electric field. A quantity of such fundamental importance has a great deal of theoretical use as might be expected. The SDC, ϵ_s , is one of the most commonly used fitting parameters in the various shell models of ionic crystals. The resultant equations are then used to predict frequency-wave number relations, $\omega(q)$, which can then be compared with the results from the scattering of thermal neutrons. The reverse process, "best fitting" of the thermal neutron data, also gives results which can be discussed in conjunction with the SDC. The characteristic constants of other kinds of models such as the polarizability in the Clausius-Mossotti solid, and the effective charge and compressibility of the Szigeti crystal also require a value of the SDC for their evaluation. In addition, there have been quantum mechanical calculations of the SDC which require comparison with experimental data.

Similar importance is ascribed to the pressure and temperature variation of the SDC. The effects on the SDC due to hydrostatic compression reflect how electron-nucleus, ion-ion, "free electron", or polar systems respond to a change in interatomic dis-

tance. The temperature derivatives contain information both on analogous crystal size effects, and those that are intrinsically thermal. The latter are particularly important in that they give a direct indication of the anharmonicity of the lattice. An accurate mapping of the SDC in the P-T plane, then, is of interest to anyone who studies solids.

Thus, it is surprising to learn from a review of the literature that though the SDC is one of the most important solid state constants, it is one of the least well-determined. A great deal of discrepancy also exists for its pressure and temperature derivatives. This work resolves a portion of the discrepancies by establishing numbers for the SDC and its pressure and temperature derivatives of the crystals LiF, NaF, NaCl, NaBr, KCl, and KBr, almost two orders of magnitude more accurately than any previously reported. For the first time, then, it is possible to closely evaluate the electrical aspects of the various models of these crystals.

This particular group of crystals was chosen in that it exists as a set of isomorphic face-centered-cubic crystals which makes it possible to correlate the dielectric properties with cation and/or anion species. Another desirable property of this set of crystals is that there are only electron-nucleus and ion-ion contributions to the SDC, which, in turn, may be separated by including refractive index measurements.

THEORY

A. The Static Dielectric Constant of Ionic Crystals

In describing the electrodynamics of systems which contain dielectrics, a convenient approach is to introduce both bound and free volume charge densities ρ' and ρ . The bound charge density is related to a macroscopic field variable through the equation:

$$\nabla \cdot \underline{P} = -\rho' \quad (1)$$

where $\underline{P}$, the polarization vector, is the dipole moment per unit volume.

Defining $\underline{E}$ to be the macroscopic field intensity, Gauss's law for dielectrics is:

$$\nabla \cdot \underline{E} = 4\pi(\rho + \rho') \quad (2)$$

Substituting Eq. (1) into Eq. (2), we have:

$$\nabla \cdot (\underline{E} + 4\pi\underline{P}) = 4\pi\rho \quad (3)$$

and the displacement vector, $\underline{D}$, is then defined to be:

$$\underline{D} = \underline{E} + 4\pi\underline{P} \quad (4)$$

The result is one of Maxwell's equations for systems containing material media:

$$\nabla \cdot \underline{D} = 4\pi\rho \quad (5)$$

Finally, the dielectric constant for isotropic media is defined as the ratio of the displacement vector to the electric field intensity, and this is represented by the equation:

$$\underline{D} = \epsilon_s \underline{E} \quad (6)$$

The constant of proportionality between the polarization vector and the electric field intensity is called the electric susceptibility, χ_e , and thus, its defining equation is:

$$\underline{P} = \chi_e \underline{E} \quad (7)$$

From Eq.s (4), (6), and (7), it is seen that

$$\epsilon_s = 1 + 4\pi\chi_e \quad (8)$$

The above formalism describes the bulk dielectric properties of isotropic solids completely. It does not, however, give any insight into the actual physical mechanisms involved in the interaction of solids with electromagnetic radiation. A complete microscopic picture, of course, is impossible, in that substances generally contain extremely large numbers of atoms or molecules. There are, however, several approximate methods for approaching this problem. A question common to all of these analyses is, What field does an atom or molecule feel? The best answer at the present time was presented by Lorentz¹ over sixty years ago. The basic idea is to write the field at an atom's center,² $\underline{E}_{loc}$, as:

$$\underline{E}_{loc} = \underline{E}_0 + \underline{E}_1 + \underline{E}_2 + \underline{E}_3 \quad (9)$$

where:

$\underline{E}_0$ = External electric field, from external charges,

$\underline{E}_1$ = Depolarization field, from polarization charges on the outer surfaces of the specimen,

$\underline{E}_2$ = Lorentz cavity field, field from polarization charges on the inside of a spherical cavity cut (as a mathematical fiction) out of the specimen with the reference atom as the center,

$\underline{E}_3$ = Field of atoms inside the cavity.

The geometry of the samples studied in this work are thin disks, and the effective electrical configuration is essentially that of a perfect parallel-plate capacitor. The above concepts apply to this problem as follows: If in the absence of a dielectric, there are surface charge densities, $\pm E'/4\pi$ on the plates, when the dielectric is inserted, an added charge density, $\pm P$, collects on the respective plates, to neutralize the polarization charge density, $\mp P$, induced at the surface of the dielectric. Thus,

$$\begin{aligned} E_0 + E_1 &= E' + 4\pi P - 4\pi P \\ &= E' \end{aligned} \quad (10)$$

which is the space average field of macroscopic theory. Next, the field due to the polarization charges on the surface of the fictitious spherical cavity is:²

$$E_2 = \frac{4\pi P}{3} \quad (11)$$

Finally, the field due to the dipoles inside the fictitious cavity is calculated, assuming that all the atoms are replaced by point dipoles parallel to each other. If the axis of the dipoles is taken as the z-axis, the field at the reference point caused by

the other dipoles of moment p_i at r_i is:

$$E_3^z = \sum_i \frac{(3p_i z_i^2 - p_i r_i^2)}{r_i^5} \quad (12)$$

For cubic symmetry:

$$\sum_i \frac{x_i^2}{r_i^2} = \sum_i \frac{y_i^2}{r_i^2} = \sum_i \frac{z_i^2}{r_i^2} \quad (13)$$

which implies that

$$E_3 = 0 \quad (14)$$

Thus

$$E_{loc} = E + \frac{4\pi P}{3} \quad (15)$$

which is known as the Lorentz relation. Over the years, this expression has received a great deal of attention. Several different approaches to obtaining the local field by simple classical methods have all resulted in the Lorentz relation.³ The same result has been obtained both by summing dipoles⁴⁻⁶ and statistical mechanical calculations.⁷ Another author⁸ has pointed out that a rigorous quantum mechanical derivation of the Lorentz local field can be made by the use of a suitable canonical transformation. In addition, it has been shown that this value for the local field gives the most consistent interpretation of refractivity^{9,10} and

photoelasticity¹¹ data. Taking the Lorentz relation to give the field at an atom, the first step can be made toward describing the dielectric constant in microscopic terms. Let us define the polarizability, α , of the spherical section mentioned above by the equation:

$$P = N \alpha E_{loc} \quad (16)$$

where N is the number of such spheres per unit volume. From Eqs. (15) and (16) we see that:

$$\frac{P}{E} = \frac{N\alpha}{1 - \frac{4\pi\alpha N}{3}} \quad (17)$$

From Eqs. (4) and (6) we know that:

$$\frac{P}{E} = \frac{\epsilon_s - 1}{4\pi} \quad (18)$$

from which we derive a macroscopic Clausius-Mossotti formula:

$$\frac{\epsilon_s - 1}{\epsilon_s + 2} = \frac{4\pi N\alpha}{3} \quad (19)$$

It is to be emphasized,³ however, that Eq. (19) has no significance from a molecular point of view. In order to derive the analogous molecular Clausius-Mossotti equation, the conditions that need to be imposed are:

1. Elastic displacement only,
2. Absence of nondipolar (short-range) interactions between molecules,

3. Isotropy of the polarizability of a molecule, and

4. Isotropy of the arrangement of the molecules.

For low frequency vibrations of crystals conditions 2 and 3 are violated and, hence, no low frequency microscopic Clausius-Mossotti formula will be written.

Writing the total polarizability as:

$$\alpha = \alpha_i + \alpha_e \quad (20)$$

where α_i and α_e , are the ionic, and electronic contributions to the polarizability of the sphere, a high frequency analog of Eq. (19) can be written as:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N \alpha_e}{3} \quad (21)$$

where n is the refractive index. This expression is known as the Lorentz-Lorenz equation. In this case, however, all but condition 2 are closely followed, and, thus, a microscopic extension of Eq. (21) can be written as:

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4}{3} N N'' [(\alpha_e^+)_a + (\alpha_e^-)_a] \quad (22)$$

where:

$$\alpha_e = N'' [(\alpha_e^+)_a + (\alpha_e^-)_a] \quad (23)$$

and N'' is the number of ion pairs per spherical volume, and $(\alpha_e^+)_a$ and $(\alpha_e^-)_a$ are the electronic polarizabilities of the positive and negative ions respectively. To treat the SDC microscopically, then, it is necessary to go to a more sophisticated model.

The first lattice dynamical model of an advanced nature was

the rigid ion model. On the basis of this model, Born¹² derived the equation:

$$\epsilon_s = n^2 + \frac{(ze)^2 N'}{\pi v_t^2 \bar{M}} \quad (24)$$

where

z = valence,

$\bar{M} = \frac{m^+ m^-}{m^+ + m^-}$, the reduced mass of the ions,

v_t = the characteristic infrared frequency, and

N' = number of ion pairs per unit volume.

The predictions from this equation are listed in Table I where they are compared to an average of the 0.01% experimental results of this work. As seen there, the model is not as successful in describing dielectric properties as it is in determining cohesive properties. The reason was apparent to several authors,¹³⁻¹⁶ including Born, himself, who noted that the effects of overlap of the ions could have quite significant effects on electrical properties of ionic crystals.

At this point, Szigeti^{17,18} made an important contribution. First, he modified the Born equation to take into account the effect of the long range interaction of transverse waves with the ions. This was done using an idea of Lyddane, Sachs, and Teller.¹⁶ Then, he added a constant, s , to indicate the deviation of the prediction of the modified Born theory from the experimentally observed SDC. The equation the Sziegeti finally arrived at is:

TABLE I Room temperature (300°K) basic data and the results of its application to the simple Born model compared to an average of the experimental results of this work.

	n^2 [42]	N' [43]	v_t [44]	$\bar{M}$ [45]	$(\epsilon_s)_{\text{Born}}$	$(\epsilon_s)_{\text{Exp.}}$
Units	—	$\times 10^{22}/\text{cm}^3$	$\times 10^{12}/\text{sec}$	$\times 10^{-24} \text{ gm}$		
LiF	1.926	6.1243	9.144	8.4384	8.342	9.0357
NaF	1.742	4.0183	7.390	17.2701	4.870	5.0720
NaCl	2.329	2.2291	4.917	23.1541	5.253	5.8945
NaBr	2.60	1.8729	4.038	29.6405	5.446	6.3965
KCl	2.173	1.6046	4.285	30.8707	4.252	4.8120
KBr	2.358	1.3910	3.444	43.5883	4.334	4.8740

$$\epsilon_s = n^2 + \left(\frac{n^2+2}{3} \right)^2 \frac{(sze)^2 N'}{\pi v_t^2 \bar{M}} \quad (25)$$

The quantity, s , then, is a measure of the effects of ion overlap on the SDC. A rather physical way of understanding s is to consider the quantity se to be an effective charge, e^* . This is then thought of as the charge of a dipole which has the same displacement as the induced dipole moment of the modified Born model, and, which must describe the total effect of the "distortion" dipole, and the modified Born dipole.

The introduction of this concept has stimulated a great deal of theoretical work. The first break through in the attempt to account for the ion overlap effects on the SDC was made by Dick and Overhauser.¹⁹

They introduced a model in which ions are replaced by a compact core and a shell containing n^+ electrons for the positive ion and n^- electrons in the case of the negative ion. The shell represents the outer electrons which, by virtue of their relatively weak binding, account for a major portion of the electronic polarizability. The core consists of the nucleus and the remaining electrons. The core and the positive (negative) ion shell are connected by a spring of constant $k^+(k^-)$. The original paper introduced two mechanisms which could be important at the ion-ion contact points. The first is a mechanical repulsion between the two shells. This is represented by a spring between the two shells which tends to displace the shells relative to the cores. The effects are

opposite for the two types of ions, tending to add to the dipole moment of the positive ion, and to subtract from the dipole moment of the negative ion. The other mechanism suggested is a redistribution of charge at the contact points. This is represented by adding a positive charge between the ions with a correspondingly increased negative charge to preserve electrical neutrality. When the lattice is polarized, these charges become skewed and contribute a dipole moment to the total picture. This added moment is known as exchange charge polarization, and the model itself is known as the exchange charge model.

Mathematically depicting the above two effects, Dick and Overhauser arrived at the equation:

$$\left(1 - \frac{e^*}{e}\right) = \frac{(r_- - r_+) B (R_o - 4 p'')}{p'' \sigma e^2} \exp - \left(\frac{R_o}{p''}\right) - \frac{6R_o}{\chi_T e} \left\{ \frac{n^+ e - D}{k^+} - \frac{n^- e + D}{k^-} \right\} \left\{ 1 + \frac{6R_o}{\chi_T} \left(\frac{1}{k^+} + \frac{1}{k^-} \right) \right\}^{-1} \quad (26)$$

where R_o is the equilibrium nearest neighbor distance, $r_{\pm}$ are the ionic radii, χ_T is the compressibility, B and p'' are the Born-Mayer parameters B and ρ , σ is the Dick and Overhauser γ which is an exchange charge weighting factor, and $-D/e$ is equal to the first term on the right hand side of the equation.

At about the same time, Hanlon and Lawson²⁰ proposed a

similar model which is essentially the exchange charge model without the exchange charge. This is what is generally known as the shell model. They arrived at the expression:

$$(1 - \frac{e^*}{e}) = \frac{f\bar{M}\Omega_R^2\{(\alpha_e^-)_a - (\alpha_e^+)_a\}/n'e^2}{1 - f\bar{M}\Omega_R^2\{(\alpha_e^-)_a - (\alpha_e^+)_a\}/n'e^2} \quad (27)$$

where f is a constant describing the difference between the mechanical and electrical forces, n' is the average number of shell electrons, and,

$$\frac{1}{\Omega_R^2} = \frac{n^2 + 2}{4\pi v_t^2(\epsilon_s + 2)} + \frac{\bar{M}}{k^+} + \frac{\bar{M}}{k^-} \quad (28)$$

Note that Eq. (27) is a function of the difference between the polarizabilities of the positive and negative ions as would be expected for a model based on the first distortion mechanism discussed in conjunction with the exchange charge model.

Cowley²¹ has given the semiclassical shell model a quantum mechanical foundation. He used first order perturbation theory under the harmonic, electrostatic and adiabatic approximations to derive the equations governing the normal modes of vibration of a crystal in which the atoms are polarizable. He found that in the dipolar approximation, the equations of motion are identical to those which are obtained for the shell model.²² Sinha²³ has recently arrived at the same results from a slightly different quantum mechanical approach.

There is one other picture of ionic crystals which should be mentioned. Born and Huang²⁴ developed a general formalism to take into account the distortion effects at the ion contact points by introducing a "deformation" dipole moment $m(r)$ associated with each nearest-neighbor bond length, r . They derived the equation for the effective charge:

$$e^* = |e| + 2 \left[\frac{dm(r)}{dr} \right]_{R_0} + \frac{4m(R_0)}{R_0} \quad (29)$$

This was put on a practical basis by Hardy.^{25,26} Generalizing the exchange charge expression of Dick and Overhauser¹⁹ to describe the distortion dipole, Hardy arrived at the equation:

$$\begin{aligned} \left(1 - \frac{e^*}{e}\right) = 2\lambda d_- \left\{ r_-^2 - r_+^2 - \frac{(d_+ - d_-)}{d_-} r_+ R_0 \right\} \left\{ \frac{1}{p''} - \frac{2}{R_0} \right\} \\ \times \exp \left(- \frac{R_0}{p''} \right) \quad (30) \end{aligned}$$

where λ is a constant in the overlap repulsion and $d_{\pm}$ are disposable parameters.

Finally, the quantum mechanical calculations of e^* by Lundqvist²⁷ and by Mitskevich²⁸ and of the value of ϵ_s for LiF by Yamashita²⁹ and by Levin and Offenbacher,³⁰ should be mentioned as practical examples of the continuing effort to place the theory of dielectrics on a firm foundation. Quite a body of less functional literature has appeared toward this end, and some of the more important of these references are listed in Appendix I.

B. The Pressure and Temperature Derivatives of the SDC.

The temperature and pressure derivatives of the SDC that this work determines for the given set of alkali halides are:

$$\frac{1}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial p} \right)_T, \quad \frac{1}{\epsilon_s} \left(\frac{\partial^2 \epsilon_s}{\partial p^2} \right)_T, \quad \frac{1}{\epsilon_s} \left(\frac{\partial^3 \epsilon_s}{\partial p^3} \right)_T, \quad \frac{1}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial T} \right)_p, \text{ and}$$

$$\frac{1}{\epsilon_s} \left(\frac{\partial^2 \epsilon_s}{\partial T^2} \right)_p.$$

These quantities are expressed in terms of experimentally determinable quantities in Appendix II.

It is of theoretical interest to examine the associated volumetric derivatives. The first step toward this end is to consider the function:

$$\epsilon_s(v, T)$$

and its total differential:

$$d\epsilon_s = \left(\frac{\partial \epsilon_s}{\partial v} \right)_T dv + \left(\frac{\partial \epsilon_s}{\partial T} \right)_v dT. \quad (31)$$

Then, the first order temperature derivative is seen to be:

$$\left(\frac{\partial \epsilon_s}{\partial T} \right)_p = v \gamma_p \left(\frac{\partial \epsilon_s}{\partial v} \right)_T + \left(\frac{\partial \epsilon_s}{\partial T} \right)_v. \quad (32)$$

where

$$\gamma_p = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p. \quad (33)$$

is the isobaric volume thermal expansion coefficient.

The first term in Eq. (32) can be evaluated using the thermodynamic relation:

$$v \left(\frac{\partial \epsilon_s}{\partial v} \right)_T = - \frac{1}{\chi_T} \left(\frac{\partial \epsilon_s}{\partial p} \right)_T \quad (34)$$

The second contribution can then be obtained via Eqs. (32) and (34) or with the help of the function:

$$\epsilon_s(p, T)$$

and its total differential:

$$d\epsilon_s = \left(\frac{\partial \epsilon_s}{\partial p} \right)_T dp + \left(\frac{\partial \epsilon_s}{\partial T} \right)_p dT \quad (35)$$

The volume independent derivative is then:

$$\left(\frac{\partial \epsilon_s}{\partial T} \right)_v = \left(\frac{\partial \epsilon_s}{\partial T} \right)_p + \frac{\gamma_p}{\chi_T} \left(\frac{\partial \epsilon_s}{\partial p} \right)_T \quad (36)$$

where

$$\chi_T = - \frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T \quad (37)$$

is the isothermal compressibility.

Analogous equations may be developed for the pressure derivative, but the volume dependent and volume independent contributions may be evaluated directly from previously calculated quantities using the thermodynamic relations:

$$\left(\frac{\partial \epsilon_s}{\partial p}\right)_v = \frac{\chi_T}{\gamma_p} \left(\frac{\partial \epsilon_s}{\partial T}\right)_v \quad (38)$$

and

$$v \left(\frac{\partial \epsilon_s}{\partial v}\right)_p = \frac{1}{\gamma_p} \left(\frac{\partial \epsilon_s}{\partial T}\right)_p \quad (39)$$

The curvature of the above quantities is also of interest, and the expressions as derived in Appendix III are:

$$\begin{aligned} \left(\frac{\partial^2 \epsilon_s}{\partial T^2}\right)_v &= \left(\frac{\partial^2 \epsilon_s}{\partial T^2}\right)_p + \frac{1}{\chi_T} \left(\frac{\partial \epsilon_s}{\partial p}\right)_T \left(\frac{\partial \gamma_p}{\partial T}\right)_p \\ &+ \left(\frac{2\gamma_p}{\chi_T}\right) \left(\frac{\partial^2 \epsilon_s}{\partial p \partial T}\right) - \frac{2\gamma_p}{\chi_T^2} \left(\frac{\partial \chi_T}{\partial T}\right)_p \left(\frac{\partial \epsilon_s}{\partial p}\right)_T \\ &- \frac{\gamma_p^2}{\chi_T^3} \left(\frac{\partial \chi_T}{\partial p}\right)_T \left(\frac{\partial \epsilon_s}{\partial p}\right)_T + \frac{\gamma_p^2}{\chi_T^2} \left(\frac{\partial^2 \epsilon_s}{\partial p^2}\right)_T, \end{aligned} \quad (40)$$

$$\begin{aligned} v^2 \left(\frac{\partial^2 \epsilon_s}{\partial v^2}\right)_T &= \frac{1}{\chi_T^2} \left(\frac{\partial^2 \epsilon_s}{\partial p^2}\right)_T \\ &- \frac{1}{\chi_T} \left(\frac{\partial \epsilon_s}{\partial p}\right)_T \left\{ \frac{1}{\chi_T^2} \left(\frac{\partial \chi_T}{\partial p}\right)_T - 1 \right\}, \end{aligned} \quad (41)$$

$$\begin{aligned}
 \left(\frac{\partial^2 \epsilon_s}{\partial p^2} \right)_v &= \left(\frac{\partial^2 \epsilon_s}{\partial p^2} \right)_T + \frac{1}{\gamma_p} \left(\frac{\partial \chi_T}{\partial p} \right)_T \left(\frac{\partial \epsilon_s}{\partial T} \right)_p \\
 &+ \frac{2\chi_T}{\gamma_p} \left(\frac{\partial^2 \epsilon_s}{\partial p \partial T} \right)_p + \frac{2\chi_T}{\gamma_p} \left(\frac{\partial \chi_T}{\partial T} \right)_p \left(\frac{\partial \epsilon_s}{\partial T} \right)_p \\
 &- \frac{\chi_T^2}{\gamma_p^3} \left(\frac{\partial \gamma_p}{\partial T} \right)_p \left(\frac{\partial \epsilon_s}{\partial T} \right)_p + \frac{\chi_T^2}{\gamma_p^2} \left(\frac{\partial^2 \epsilon_s}{\partial T^2} \right)_p
 \end{aligned} \tag{42}$$

and

$$\begin{aligned}
 \left(\frac{\partial^2 \epsilon_s}{\partial v^2} \right)_p &= \frac{1}{\gamma_p^2 v^2} \left(\frac{\partial^2 \epsilon_s}{\partial T^2} \right)_p \\
 &- \frac{1}{\gamma_p v^2} \left(\frac{\partial \epsilon_s}{\partial T} \right)_p \left\{ \frac{1}{\gamma_p} \left(\frac{\partial \gamma_p}{\partial T} \right)_p + 1 \right\}
 \end{aligned} \tag{43}$$

It is also of interest to evaluate the pressure and temperature derivatives of the polarizability. This is done by differentiating the macroscopic Clausius-Mossotti relation given by Eq. (19). The first temperature derivative is:

$$\frac{1}{(\epsilon_s - 1)(\epsilon_s + 2)} \left(\frac{\partial \epsilon_s}{\partial T} \right)_p = \frac{1}{3} \left\{ \frac{1}{N} \left(\frac{\partial N}{\partial T} \right)_p + \frac{1}{\alpha} \left(\frac{\partial \alpha}{\partial T} \right)_p \right\} \tag{44}$$

Noting that:

$$\frac{1}{N} \left(\frac{\partial N}{\partial T} \right)_P = - \gamma_P \quad (45)$$

and using an expression for the polarizability analogous to Eq. (32), we find three contributions to the temperature derivative of the SDC on the basis of the Clausius-Mossotti equation:

$$\frac{1}{(\epsilon_S - 1)(\epsilon_S + 2)} \left(\frac{\partial \epsilon_S}{\partial T} \right)_P = \frac{1}{3} \left\{ \frac{1}{\alpha} \left(\frac{\partial \alpha}{\partial T} \right)_V + \frac{v \gamma_P}{\alpha} \left(\frac{\partial \alpha}{\partial v} \right)_T - \gamma_P \right\} \quad (46)$$

the thermal and volumetric effects on the polarizability, and a purely volumetric effect. The various factors can be evaluated³¹ with the help of the pressure derivative:

$$\frac{1}{(\epsilon_S - 1)(\epsilon_S + 2)} \left(\frac{\partial \epsilon_S}{\partial p} \right)_T = \frac{1}{3} \left\{ \chi_T + \frac{1}{\alpha} \left(\frac{\partial \alpha}{\partial p} \right)_T \right\} \quad (47)$$

Using the thermodynamic relation:

$$- \frac{1}{\chi_T} \left(\frac{\partial \alpha}{\partial p} \right)_T = v \left(\frac{\partial \alpha}{\partial v} \right)_T \quad (48)$$

and rearranging terms, we obtain:

$$\frac{1}{(\epsilon_S - 1)(\epsilon_S + 2)} \left(\frac{\partial \epsilon_S}{\partial p} \right)_T = - \frac{1}{3} \frac{\chi_T}{\gamma_P} \left\{ \frac{v \gamma_P}{\alpha} \left(\frac{\partial \alpha}{\partial v} \right)_T - \gamma_P \right\} \quad (49)$$

Comparing this with Eq. (46) we see that the three contributions can be separated.

Similarly, three contributions to the pressure derivatives can be obtained by expanding Eq. (47) to read:

$$\frac{1}{(\epsilon_s - 1)(\epsilon_s + 2)} \left(\frac{\partial \epsilon_s}{\partial p} \right)_T = \frac{1}{3} \left\{ \chi_T - \frac{v \chi_T}{\alpha} \left(\frac{\partial \alpha}{\partial v} \right)_p + \frac{1}{\alpha} \left(\frac{\partial \alpha}{\partial p} \right)_v \right\} \quad (50)$$

In this case, the quantities in the parentheses may be determined from:

$$v \left(\frac{\partial \alpha}{\partial v} \right)_p = \frac{1}{\gamma_p} \left(\frac{\partial \alpha}{\partial T} \right)_p \quad (51)$$

and

$$\left(\frac{\partial \alpha}{\partial p} \right)_v = \frac{\chi_T}{\gamma_p} \left(\frac{\partial \alpha}{\partial T} \right)_v \quad (52)$$

Also, the curvature of the volume dependent and independent terms can be obtained from expressions analogous to Eqs. (40) - (43) by substituting $\alpha \rightarrow \epsilon_s$ everywhere. The second order derivatives necessary for these calculations are:

$$\begin{aligned} \frac{1}{\alpha} \left(\frac{\partial^2 \alpha}{\partial T^2} \right)_p &= \frac{3}{(\epsilon_s - 1)(\epsilon_s + 2)} \left(\frac{\partial^2 \epsilon_s}{\partial T^2} \right)_p + \left(\frac{\partial \gamma_p}{\partial T} \right)_p \\ &+ \frac{1}{\alpha^2} \left(\frac{\partial \alpha}{\partial T} \right)_p^2 - \frac{3(2\epsilon_s + 1)}{(\epsilon_s + 2)^2 (\epsilon_s - 1)^2} \left(\frac{\partial \epsilon_s}{\partial T} \right)_p^2 \end{aligned} \quad (53)$$

and

$$\begin{aligned} \frac{1}{\alpha} \left(\frac{\partial^2 \alpha}{\partial p^2} \right)_T &= \frac{3}{(\epsilon_s - 1)(\epsilon_s + 2)} \left(\frac{\partial^2 \epsilon_s}{\partial p^2} \right)_T - \left(\frac{\partial \chi_T}{\partial p} \right)_T \\ &+ \frac{1}{\alpha^2} \left(\frac{\partial \alpha}{\partial p} \right)_T^2 - \frac{3(2\epsilon_s + 1)}{(\epsilon_s + 2)^2 (\epsilon_s - 1)^2} \left(\frac{\partial \epsilon_s}{\partial T} \right)_p^2 \end{aligned} \quad (54)$$

The above thermodynamic separations are of physical as well as mathematical significance, and it is convenient to discuss the microscopic theories in the same manner.

1. The Volume Dependent Effect

Since the volume dependent effect is concerned with the change of the SDC with a variation in interionic distance only, it is of interest to determine the predictions of the simple Born model. Differentiating Eq. (24) with respect to volume, we obtain:

$$v \left(\frac{\partial \epsilon_s}{\partial v} \right)_T = - \frac{1}{\chi_T} \left(\frac{\partial n^2}{\partial p} \right)_T - (1 - 2\gamma_{TO}) (\epsilon_s - n^2) \quad (55)$$

where

$$\gamma_{TO} = - \frac{v}{v_t} \left(\frac{\partial v_t}{\partial v} \right)_T \quad (56)$$

is the Gruneisen parameter of the long wavelength transverse optical mode. As seen in Tables II and XIX, the predictions of this model are fairly good considering its simplicity. From our discussion of the SDC itself, however, we would expect that this formulation is

TABLE II. Pressure and temperature variation of optical and infrared properties of ionic crystals.

	LiF	NaF	NaCl	NaBr	KCl	KBr
γ_{TO}	^[50] 2.15	^[50] 2.40 ^[52]	^[52] 2.10	^[52] 1.25	^[51] 2.68	^[51] 2.71
$\left(\frac{\partial n}{\partial p}\right)_T \left(10^{-12} \frac{\text{cm}^2}{\text{dy}}\right)$	^[53] .1980	^[53] .2722	^[53] 1.170	^[54] 1.571	^[53] 1.816	^[53] 2.438
$v \left(\frac{\partial \epsilon_s}{\partial v}\right)_T = \text{RHS Eq. (55)}$ Born	23.10	12.32	10.53	4.71	10.59	10.05
$\left(\frac{\partial n}{\partial T}\right)_p (10^{-5}/^\circ\text{K})$ ^[55]	-1.6	-2.2	-3.7	-4.1	-3.6	-4.0
$v \left(\frac{\partial n}{\partial v}\right)_T$	-.1289	-.1257	-.2765	-.3064	-.3115	-.3566
$\left(\frac{\partial n}{\partial T}\right)_v (10^{-5}/^\circ\text{K})$	-.269	-.952	-.361	-.193	-.114	-.204

inadequate in two respects. First, the long range interaction between the transverse waves and the ions is neglected, and second, the short range effects of overlap are omitted.

The next step, then, is to incorporate the former, and evaluate the effects of latter using the Szigeti relation, Eq. (25). Differentiating this equation we obtain:

$$\frac{v}{e^*} \left(\frac{\partial e^*}{\partial v} \right)_T = - \frac{1}{2\chi_T} \left\{ \frac{1}{(\epsilon_s - n^2)} \left[\left(\frac{\partial \epsilon_s}{\partial p} \right)_T - \left(\frac{\partial n^2}{\partial p} \right)_T \right] - \frac{2}{(n^2 + 2)} \left(\frac{\partial n^2}{\partial p} \right)_T + \chi_T (2\gamma_{TO} - 1) \right\} \quad (57)$$

The quantity $(\partial e^* / \partial v)_T$ is rather interesting physically in that it would be expected to be positive since the effects of overlap should be accentuated as the ions impinge on one another.

Fuchs³² has evaluated this term on the basis of the model of Dick and Overhauser,¹⁹ arriving at the expression:

$$\frac{v}{e^*} \left(\frac{\partial e^*}{\partial v} \right)_T = - \frac{R_o}{3p''} \frac{\left(\frac{R_o}{p''} - 5 \right) \frac{D}{e}}{\left(\frac{R_o}{p''} - 4 \right) \left(1 + \frac{D}{e} \right)} \quad (58)$$

This quantity can also be evaluated on the basis of the deformation dipole models of Hardy^{25,26} and Mitskevich.²⁸ This was done by Barron³³ who arrived at the equation:

$$\frac{v}{e^*} \left(\frac{\partial e^*}{\partial v} \right)_{T=0} = \frac{1 - \frac{e^*}{e}}{\frac{e^*}{e}} \left\{ \xi - \frac{2}{(\xi-2)} \right\} \quad (59)$$

where $\xi = R_0/p''$ for Hardy and ξ was calculated quantum mechanically by Mitskevich.

In addition, Yamashita³⁴ has made a purely quantum mechanical calculation of this effect.

2. The Volume Independent Effect

A procedure analogous to the above cannot fruitfully be carried out because the data necessary for determining $(\partial \epsilon_s / \partial T)_V$ on the basis of the models considered thus far has not been determined very accurately. This is particularly disappointing in that it would be interesting to determine how well the quasi-harmonic approximation, which is intrinsic to all of the above models, can account for purely thermal effects on the SDC. Some light can be shed on this issue, though, by developing a formalism to evaluate anharmonic effects explicitly.

Frank³⁵ was the first to show that anharmonic potentials could produce a purely temperature effect on the polarizability. Several years later, Slater³⁶ developed a quantitative theory which included a small fourth order contribution to the parabolic potential energy. His potential was of the form:

$$V(x) = Ax^2 + Bx^4 - eEx. \quad (60)$$

This theory fails in that for all physically reasonable cases, it predicts a negative value for $(\partial \epsilon_s / \partial T)_V$, and as will be seen, this

term is positive for most of the alkali halides.

Looking elsewhere for the solution, Fuchs³² included higher order terms in the expansion of the dipole moment by considering the dipole moment:

$$\mu = e^* x + cx^3 \quad (61)$$

which requires the modified form of the potential energy:

$$V(x) = Ax^2 + Bx^4 - e^* Ex - cEx^3. \quad (62)$$

He found that the additional term also gives a negative contribution to $(\partial \epsilon_s / \partial T)_V$. Thus, as might be expected, a more complete description of the relevant lattice dynamics is required. The necessary formalism has been supplied by Szigeti.^{37,38} He writes the dipole moment up to third order in the normal coordinates, Q , as

$$M = \alpha_0 Q_0 + \sum_{ij} \beta_{ij} Q_i Q_j + \sum_{ijk} \gamma_{ijk} Q_i Q_j Q_k \quad (63)$$

where α_0 , β_{ij} , and γ_{ijk} are constants. He also writes the lattice potential energy to fourth order with constants b_{ijk} and c_{ijkl} as:

$$W = \frac{1}{2} \sum_i \omega_i^2 Q_i^2 + \sum_{ijk} b_{ijk} Q_i Q_j Q_k + \sum_{ijkl} c_{ijkl} Q_i Q_j Q_k Q_l. \quad (64)$$

Writing the Hamiltonian and applying perturbation theory, Szigeti arrived at:

$$\begin{aligned} \epsilon_s - n^2 = & \frac{4\pi\alpha_o^2}{V\omega_o^2} + \frac{4\pi\hbar}{V} \sum_{ij} \left(\beta_{ij} - \frac{\alpha_o b_{oij}}{\omega_o^2} \right)^2 \\ & \times \frac{1}{2\omega_i \omega_j} \left(\frac{1 + \bar{n}_i + \bar{n}_j}{\omega_i + \omega_j} + \frac{\bar{n}_j - \bar{n}_i}{\omega_i - \omega_j} \right) \\ & + \frac{8\pi\hbar}{V} \frac{\alpha_o}{\omega_o^2} \sum_i \left(\gamma_{oii} - \frac{\alpha_o c_{ooii}}{\omega_o^2} \right) \frac{\bar{n}_i + \frac{1}{2}}{\omega_i} \end{aligned} \quad (65)$$

where

$$\bar{n}_i = \frac{1}{e^{\hbar\omega_i/kT} - 1} \quad (66)$$

It is seen that the first term

$$\eta \equiv \frac{4\pi\alpha_o^2}{V\omega_o^2} \quad (67)$$

is the harmonic contribution to the ionic dielectric constant, and the remainder of the terms describe the effects of the anharmonicities. Fuchs³² points out the relationship between γ_{oii} and c of Eq. (61), and between c_{ooii} and B of Eq. (62). The last term in Eq. (65) then corresponds to the more classical result of Eqs. (61) and (62). He goes on to show that this term correspondingly gives a negative contribution to $(\partial\epsilon_s/\partial T)_V$ in that $\gamma_{oii} < 0$ and $c_{ooii} > 0$, and $\bar{n}_i$ increases with temperature.

The second term on the right hand side of Eq. (65), however, has no analogy in the classical formulation because it contains third order anharmonic potential constants b_{oij} and second-order dipole-moment constants β_{ij} . Looking closely at the coefficient, we see that this term contributes significantly when there is a large difference in frequencies. Under these conditions, it is seen that it also has a positive temperature coefficient, and thus the whole term contributes positively to $(\partial\epsilon_s/\partial T)_V$. Hence, it is the interaction between the acoustical and optical modes which gives the positive volume independent temperature coefficient observed in most of the alkali halides.

In addition, Fuchs shows that:

$$\frac{\alpha_o}{\omega_o^2} \approx (\epsilon_s + 2) \quad (68)$$

which means that the last term on the right hand side of Eq. (65) increases as the SDC increases. It is thus possible that this term could overtake the positive contribution to $(\partial\epsilon_s/\partial T)_V$ at a high enough value of the SDC. Unfortunately, nothing more than a qualitative picture of this equation exists at the present time.

All is not lost, however, in that Szigeti³⁹ has shown how to evaluate the anharmonic contribution to the SDC itself from this formalism. First, he writes Eq. (65) in the form:

$$\epsilon_s - n^2 = \eta + G \quad (69)$$

where η was defined in Eq. (67). G , then, represents the lowest

order anharmonic contribution to the ionic dielectric constant. He then writes Eq. (66) in the high temperature limit as:

$$\bar{n}_i = \frac{kT}{K\omega_i} - \frac{1}{2} \quad (70)$$

Substituting Eq. (70) into (65), he writes:

$$G = HT \quad (71)$$

where:

$$H = \frac{4\pi K}{V} \sum_{ij} \left(\beta_{ij} - \frac{\alpha_o^b o_{ij}}{\omega_o^2} \right)^2 \frac{1}{(\omega_i \omega_j)^2} + \frac{8\pi h \alpha_o}{V \omega_i^2} \sum_i \left(\gamma_{oii} - \frac{\alpha_o^c o_{oii}}{\omega_o^2} \right) \frac{1}{\omega_i^2} \quad (72)$$

Looking over the various contributions to Eq. (72) Szigeti argues that n is a unique function of a carefully defined volume, V , H is a constant, and G is effectively a unique function of T . He then arrives at the relation:

$$G = T \left\{ \left(\frac{\partial \epsilon_s}{\partial T} \right)_V - \left(\frac{\partial n^2}{\partial T} \right)_V \right\} \quad (73)$$

Eq. (73) then gives the anharmonic contribution, G , to the lattice contribution of the SDC, the relative importance of which gives a rather good indication of the applicability of the quasi-harmonic approximation to our problem.

EXPERIMENTAL PROCEDURE

A. The Static Dielectric Constant

The details of the determination of the SDC of the chosen alkali halides are given in References 74, 75, and 76.

B. The Pressure and Temperature Derivatives of the SDC

1. Samples

In this segment of the research, it is desirable to have electrodes in direct contact with the samples. No geometrical measurements are required in that only relative changes in capacitance are determined, and, thus, the only ambiguities which arise from plated electrodes for this phase of the research are those associated with the electrode-crystal interface⁴⁰ or electrode-crystal interactions.⁴¹ Uncertainties related to the former problem can be reduced greatly by evaporating metal electrodes onto the surface of the sample, and those associated with the latter by using gold as the metal. The samples investigated were some of those described in Reference 75. The gold evaporations were done in a manner similar to the aluminum evaporations described in Reference 77. The differences are that in this case, the samples were outgassed at 180°C instead of 150°C, and some films were made approximately 2000Å thick and others 200Å.

2. Pressure Derivatives

A block diagram of the apparatus used to measure the room

temperature (308°K) pressure derivatives of the SDC is shown in Figure 1. The Vascomax 300 maraging steel pressure bomb is the vessel referred to in Reference 77. A cross section of the bomb is shown in Figure 2. In this part of the experiment it was used simultaneously as a 0.01% pressure gage and pressure vessel by using one sample space for a CaF_2 pressure standard, and the remaining three for samples. The transformer ratio arm bridge which was mentioned in Reference 77 was used to monitor the capacitance changes of the CaF_2 pressure standard. The temperature of the bomb was controlled to within 0.0005 C° during the period of a run by means of a feedback temperature controller. Further details of the pressure vessel, transformer ratio arm bridge, and temperature controller will be forthcoming shortly in a Case Western Reserve University doctoral dissertation by Carl Andeen. The General Radio Type 1620-A capacitance measuring assembly which was used to measure the capacitance changes of the samples to one part in 10^7 is described in detail in References 74, 75, and 76. The pressure was generated by an Amnico 0-40,000 psi pump of standard piston-ball check design, and the pressure fluid used was Simplex projector oil which is a highly refined petroleum oil.

3. Temperature Derivatives

Zero pressure temperature derivatives of capacitance were obtained using the apparatus depicted in the block diagram in Figure 3. Low temperatures were achieved in a Cryogenics Associates, Inc. CT-14 temperature dewar, and the temperature was controlled

FIGURE 1. Block Diagram of the Apparatus used for the Measurement of the Room Temperature (308°K) Pressure Derivatives of the SDC.

FIGURE 2. Maraging Steel Bomb and Associated Parts.

a) BNC Connectors	g) Sample
b) Maraging Steel Collar	i) Brass Can
c) O=Ring	j) Glass-encapsulated Thermistor
c) Beryllium Copper Armor Ring	k) Heating Resistor
e) Aluminum Jacket	l) Maraging Steel Closure Plug
f) High Pressure Electrical Lead Through	

FIGURE 3. Block Diagram of the Apparatus Used for the Measurement of the Zero Pressure Temperature Derivatives of the SDC.

using feedback concepts. The sample holder was made of beryllium copper, and is of similar design to the maraging steel bomb described above. Temperatures were determined by measuring the resistance of a platinum resistance thermometer, using the 27 Hz bridge mentioned in References 75 and 76 and are thought to be accurate to within ± 0.1 C°. Further details of this apparatus will also be given in the forthcoming thesis by Andeen. Again, the capacitance changes were measured to one part in 10^7 using the General Radio Type 1620-A capacitance measuring assembly.

RESULTS

A. The Static Dielectric Constant

The results for the SDC of the chosen alkali halides are listed and discussed from an experimental point of view in Reference 75.

B. The Pressure Derivatives of the SDC

1. Raw data

Typical pressure versus capacitance data is shown in Figure 4. The numbers for each pressure run were fitted to a cubic equation of the form:

$$C/C_0 = 1 - A_1p + A_2p^2 + A_3p^3, \quad (74)$$

where C_0 is the zero pressure, 308°K capacitance, by the method of least squares using a Univac 1108 computer. The results are listed in Table III. The estimated experimental uncertainties associated with A_1 , A_2 , and A_3 are 0.1%, 1%, and 10%, respectively, for NaCl, and KCl. The linear term for LiF and NaF is correct to about 0.1% also, but, due to the rather small magnitude of the quadratic and cubic terms, their experimental uncertainties are about 3% and 30% respectively. Due to the softness and more hygroscopic nature of KBr and NaBr, additional ambiguities place the uncertainty on A_1 , A_2 , and A_3 for these crystals at about 0.2%, 2%, and 20% respectively. Comments similar to those made for the

FIGURE 4.

Plot of Pressure Versus Capacitance Change for the Alkali Halides.

TABLE III Coefficients in the equation: $C/C_o = 1 - A_1p + A_2p^2 - A_3p^3$
 where p is in units of dynes/cm².

			A_1	A_2	A_3
Units	Identification	SDC	$10^{-12} \frac{\text{cm}^2}{\text{dy}}$	$10^{-22} \frac{\text{cm}^2}{\text{dy}}$	$10^{-33} \frac{\text{cm}^2}{\text{dy}}$
LiF	II (H)	9.0357	5.591	0.477	0.44
	IV (O)	9.0357	5.603	0.482	0.18
NaF	I (H)	5.0722	6.121	0.698	0.93
	V (O)	5.0719	6.118	0.677	0.15
NaCl	VIII (O)	5.8954	11.802	2.772	5.96
	III (H)	5.8952	11.798	2.798	6.58
	IX (O)	5.8952	11.798	2.771	6.10
	VIII (H)	5.8944	11.791	2.774	6.12
NaBr	I (H)	6.3972	14.401	4.190	10.29
	III (O)	6.3966	14.424	4.858	21.15

TABLE III -- Continued

			A_1	A_2	A_3
Units	Identification	SDC	$10^{-12} \frac{\text{cm}^2}{\text{dy}}$	$10^{-22} \frac{\text{cm}^2}{\text{dy}}$	$10^{-33} \frac{\text{cm}^2}{\text{dy}}$
KCl	XI (O)	4.8126	12.937	3.887	7.49
	IV (H)	4.8115	12.985	4.156	12.15
	III (H)	4.8113	12.927	3.939	9.22
	VI (O)	4.8179	13.001	4.165	13.97
KBr	VII (O)	4.8762	14.776	5.580	22.07
	I (H)	4.8738	14.722	5.513	18.57
	VIII (O)	4.8758	14.802	5.788	22.73

SDC related to the effects of random trace impurities can be made for the pressure derivatives. Even though the SDC of LiF and NaF from the two sources, the Harshaw Chemical Co. and Optovac, Inc., were very uniform, the losses were not, being 40 and 87 for Harshaw and Optovac LiF and 35 and 40 for H and O NaF, respectively. The variation of the pressure derivatives of the SDC are directly correlated with the trends in the loss for the two samples.

In the case of KCl, the largest pressure derivative occurs for the sample with the greatest value of the SDC. KCl samples XI and III show a corresponding decrease of pressure derivative with SDC, but sample IV does not fit into the scheme. For KBr, the two samples with the largest SDC also show the largest pressure derivatives, but the results for NaBr seem to be opposite, however, this is based on only two samples. In addition, it is noted that the most uniform values of the pressure derivatives were obtained for NaCl which were correspondingly the most uniform samples taking both SDC and loss into account.

The effects of electrode thickness on the pressure derivatives were investigated by making the films on NaCl sample VIII about 2000 Å thick while all of the others were approximately 20000 Å thick. The effects appear to be negligible at the level of the current investigation.

The coefficients listed in Table III were averaged, and the zero pressure derivatives of the capacitance obtained from:

$$\frac{1}{C_0} \left(\frac{\partial C}{\partial p} \right)_T = - \bar{A}_1, \quad (75a)$$

$$\frac{1}{C_o} \left(\frac{\partial^2 C}{\partial p^2} \right)_T = 2\bar{A}_2 \quad (75b)$$

and

$$\frac{1}{C_o} \left(\frac{\partial^3 C}{\partial p^3} \right)_T = -6\bar{A}_3 \quad (75c)$$

The results of these calculations are listed in Table IV.

2. Data Reduction

The basic data necessary for transforming the pressure derivatives of capacitance to the pressure derivatives of the SDC are listed in Table V. The isothermal compressibilities of all samples except LiF are the temperature corrected average of the values tabulated by Roberts and Smith⁵⁹ and by Leibfreid and Ludwig.⁶⁰ The value of χ_T for LiF is a temperature corrected average of the values given by Miller and Smith⁶¹ and by Leibfried and Ludwig.⁶⁰ The values for the first isothermal pressure derivatives are obtained from the references given in Table V. The expression for the second isothermal pressure derivative in terms of the isothermal bulk modulus,

$$B_T = -v \left(\frac{\partial p}{\partial v} \right)_T = \frac{1}{\chi_T} \quad (76)$$

is

$$\left(\frac{\partial^2 \chi_T}{\partial p^2} \right)_T = \frac{2}{B_T^3} \left(\frac{\partial B_T}{\partial p} \right)_T^2 - \frac{1}{B_T^2} \left(\frac{\partial^2 B_T}{\partial p^2} \right)_T \quad (77)$$

The quantities on the right hand side of Eq. (77) have been evaluated for AgBr⁶⁴ for which it is found that the second term is 10% of the first. In measurements of the pressure derivatives of the elastic

TABLE IV Zero pressure logarithmic pressure derivatives
of the capacitance of the chosen alkali halides.

	$\frac{1}{C_o} \left(\frac{\partial C}{\partial p} \right)_{T,p=0}$	$\frac{1}{C_o} \left(\frac{\partial^2 C}{\partial p^2} \right)_{T,p=0}$	$\frac{1}{C_o} \left(\frac{\partial^3 C}{\partial p^3} \right)_{T,p=0}$
Units	$10^{-12} \frac{\text{cm}^2}{\text{dy}}$	$10^{-22} \left(\frac{\text{cm}^2}{\text{dy}} \right)^2$	$10^{-33} \left(\frac{\text{cm}^2}{\text{dy}} \right)^3$
LiF	- 5.597	0.959	- 1.86
NaF	- 6.120	1.375	- 3.26
NaCl	-11.798	5.558	- 37.12
NaBr	-14.413	9.048	- 94.31
KCl	-12.950	7.988	- 57.72
KBr	-14.767	11.253	-126.75

TABLE -- V. Basic data used in the reduction of room temperature (308°K) pressure and temperature derivatives

Quantity Units	LiF	NaF	NaCl	NaBr	KCl	KBr
χ_T $10^{-12} \frac{\text{cm}^2}{\text{dy}}$	1.5359	2.1656	4.2308	5.1269	5.8302	6.8367
$(\partial \chi_T / \partial T)_P$ $10^{-15} \frac{\text{cm}^2}{\text{dy} (^\circ\text{K})}$	.9074	1.2396	3.0549	3.3700	4.2411	4.6334
$(\partial \chi_T / \partial p)_T$ $10^{-24} \left(\frac{\text{cm}^2}{\text{dy}} \right)^2$	[59] -11.53	[57] -25.23	[58] -99.68	[59] -137.6	[58] -183.1	[59] -255.4
γ_P $10^{-5} / ^\circ\text{K}$	10.35	9.925	12.075	12.75	11.19	11.79
$(\partial \gamma_P / \partial T)_P$ $10^{-7} / ^\circ\text{K}^2$	1.47	1.23	.796	.6	.571	.649

TABLE V'- Continued

Quantity Units	LiF	NaF	NaCl	NaBr	KCl	KBr
$(\partial^2 \chi / \partial p^2)_T$ $10^{-36} \left(\frac{\text{cm}^2}{\text{dy}} \right)^3$	173	588	4697	7386	11500	19100

constants, it is found that the curvature of the transit time as a function of pressure is much less in the alkali halides than for AgBr and, thus, the approximation is made that:

$$\left(\frac{\partial^2 x_T}{\partial p^2}\right)_T = \frac{2}{B_T^3} \left(\frac{\partial B_T}{\partial p}\right)_T^2 = \frac{2}{x_T} \left(\frac{\partial x_T}{\partial p}\right)_T^2 \quad (78)$$

and the results are listed in Table V.

The pressure derivatives were calculated using the data of Table V and the equations of Appendix II and listed in Table VI. The results are to be compared with the values of previous workers which are listed in Table VII. It is noted that the capacitance derivatives in every case agree well with the work of Jones.⁶⁵ The dielectric constant derivatives do not agree well, however, implying that there is a difference in the basic data used to reduce the capacitance numbers. It appears, then, that choice of support data is in part responsible for the differences between our numbers and those in the literature. Another difference inherent in our data is the use of higher order terms to describe the variation of capacitance, and, hence, the SDC with pressure. The first derivative at zero pressure obtained in this manner would certainly be higher than for a smoothed linear fit to all of the data. The agreement with Jones, who was the only other worker to report curvature in this manner, tends to substantiate this hypothesis.

TABLE VI. Pressure Derivatives of the SDC of Some Alkali Halides.

	$\frac{1}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial p} \right)_T$	$\left(\frac{\partial \epsilon_s}{\partial p} \right)_T$	$\left(\frac{\partial n^2}{\partial p} \right)_T$	$\frac{1}{\epsilon_s} \left(\frac{\partial^2 \epsilon_s}{\partial p^2} \right)_T$	$\left(\frac{\partial^2 \epsilon_s}{\partial p^2} \right)_T$	$\frac{1}{\epsilon_s} \left(\frac{\partial^3 \epsilon_s}{\partial p^3} \right)_T$	$\left(\frac{\partial^3 \epsilon_s}{\partial p^3} \right)_T$
Units	$10^{-12} \left(\frac{\text{cm}^2}{\text{dy}} \right)$	$10^{-12} \left(\frac{\text{cm}^2}{\text{dy}} \right)$	$10^{-12} \left(\frac{\text{cm}^2}{\text{dy}} \right)$	$10^{-24} \left(\frac{\text{cm}^2}{\text{dy}} \right)^2$	$10^{-24} \left(\frac{\text{cm}^2}{\text{dy}} \right)$	$10^{-36} \left(\frac{\text{cm}^2}{\text{dy}} \right)$	$10^{-36} \left(\frac{\text{cm}^2}{\text{dy}} \right)$
LiF	- 5.085	-45.95	0.550	86.6	782.7	- 1612	- 14560
NaF	- 5.398	-27.38	0.718	120.8	612.7	- 2634	- 13400
NaCl	-10.388	-61.23	3.571	491.3	2895.8	- 32200	-190000
NaBr	-12.704	-81.26	5.066	812.6	5197.5	- 85600	-547000
KCl	-11.006	-52.96	5.354	691.2	3326.0	- 47400	-228000
KBr	-12.488	-60.87	7.487	978.1	4767.2	-110000	-534000

TABLE VII. Literature Values of the Pressure Derivatives of the SDC.

	[65]	[65]	[65]	[65]	[66]	[67]	[68]	[69]
	$\frac{1}{C_o} \left(\frac{\partial C}{\partial p} \right)_T$	$\frac{1}{C_o} \left(\frac{\partial^2 C}{\partial p^2} \right)_T$	$\frac{1}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial p} \right)_T$	$\frac{1}{\epsilon_s} \left(\frac{\partial^2 \epsilon_s}{\partial p^2} \right)_T$	$\frac{1}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial p} \right)_T$	$\frac{1}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial p} \right)_T$	$\frac{1}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial p} \right)_T$	$\frac{1}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial p} \right)_T$
Units	$10^{-12} \left(\frac{\text{cm}^2}{\text{dy}} \right)$	$10^{-22} \left(\frac{\text{cm}^2}{\text{dy}} \right)^2$	$10^{-12} \left(\frac{\text{cm}^2}{\text{dy}} \right)$	$10^{-24} \left(\frac{\text{cm}^2}{\text{cy}} \right)^2$	$10^{-12} \left(\frac{\text{cm}^2}{\text{dy}} \right)$	$10^{-12} \left(\frac{\text{cm}^2}{\text{dy}} \right)$	$10^{-12} \left(\frac{\text{cm}^2}{\text{dy}} \right)$	$10^{-12} \left(\frac{\text{cm}^2}{\text{dy}} \right)$
LiF	- 5.42	.924	- 4.93	46.	- 3.8	-4.23	- 3.4	- 4.48
NaF	- 5.97 (25°C)	.84 (25°C)	- 5.06 (25°C)	70.	- 5.3	—	—	—
NaCl	-11.51	4.0	-10.3	330.	- 9.2	-9.24	- 9.80	- 9.80
NaBr	-14.27	6.64	-12.6	584.	-11.9	—	—	—
KCl	-12.69	5.81	-10.69	498.	-10.0	-9.92	-10.1	-10.5
KBr	-14.20	7.2	-11.92	604.	-11.5	-9.91	-13.4	-11.7

C. The Temperature Derivatives of the SDC

1. Raw Data

Temperature versus capacitance data for LiF and NaBr is plotted in Figure 5. All of the rest of the samples generated curves which fit between these bounds. As seen in Figure 5, data was taken from 80°K to room temperature. All of the data for an individual sample did not lend itself well to a power series fit, and, thus, only the data from 200-300°K was fitted to the equation:

$$C/C_o = 1 + B_1(T-T_o) + B_2(T-T_o)^2 \quad (79)$$

where $T_o = 308^\circ\text{K}$ and T is the absolute temperature. It is to be emphasized that this power series has no significance very far beyond the region 200-300°K. The coefficients B_1 and B_2 for each sample are listed in Table VIII. The temperature data was fitted only to a second order polynomial because the accuracy of the temperature values was not sufficient to predict reliable third order coefficients. The experimental uncertainty is approximately 0.2% for B_1 and about 20% for B_2 . The 308°K temperature derivatives were then obtained from the equation:

$$\frac{1}{C_o} \left(\frac{\partial C}{\partial T} \right)_{\substack{p=0 \\ T=308^\circ\text{K}}} = B_1 \quad (80a)$$

and

FIGURE 5. Plot of Temperature Versus Capacitance Change for the Alkali Halides.

TABLE-VIII. The Coefficients in the Equation: $\frac{C}{C_0} = 1 + B_1(T-T_0) + B_2(T-T_0)^2$
and the Related Temperature Derivatives of the Capacitance.

	Identification	B_1	B_2	$\frac{1}{C_0} \left(\frac{\partial C}{\partial T} \right)_p$	$\frac{1}{C_0} \left(\frac{\partial^2 C}{\partial T^2} \right)_p$
Units	—	$10^{-5}/^{\circ}\text{K}$	$10^{-7}/(^{\circ}\text{K})^2$	$10^{-5}/^{\circ}\text{K}$	$10^{-7}/(^{\circ}\text{K})^2$
LiF	II (H)	30.41	0.79	30.41	1.59
NaF	I (H)	31.56	1.31	31.56	2.61
NaCl	VIII (O) Table II	35.62	1.41	35.62	2.82
NaBr	II (H) I	37.03 37.03	1.43 1.44	37.03	2.87
KCl	IV (H)	33.21	1.60	33.21	3.20
KBr	IV (H)	33.75	1.63	33.75	3.26

$$\frac{1}{C_0} \left(\frac{\partial^2 C}{\partial T^2} \right)_{\substack{p=0 \\ T=308^\circ K}} = 2B_2 \quad (80b)$$

The values of these derivatives are also listed in Table VIII.

2. Data Reduction

The data necessary for the transformation of capacitance to SDC temperature derivatives are given in Table V. The thermal expansion coefficients and their temperature derivatives were obtained from graphical analyses of the numbers given by James and Yates,⁵⁷ Henglein,⁶² and Yates and Panter.⁶³

The $p=0$, $308^\circ K$ temperature derivatives of the SDC were calculated using the data from Tables V and VIII and the equations of Appendix II. The results are listed in Table IX. Values from the literature are listed in Table X. It is seen that the results of this work compare well with the most recent results, those of Lowndes and Martin.⁶⁶

TABLE IX. Temperature Derivatives of the Dielectric Constants of Some Alkali Halides.

	$\frac{1}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial T} \right)_p$	$\left(\frac{\partial \epsilon_s}{\partial T} \right)_p$	$\left(\frac{\partial^2 \epsilon_s}{\partial T^2} \right)_p$	$\frac{1}{\epsilon_s} \left(\frac{\partial^2 \epsilon_s}{\partial T^2} \right)_p$	$\left(\frac{\partial^2 \epsilon_s}{\partial T^2} \right)_p$
Units	$10^{-5}/^{\circ}\text{K}$	$10^{-5}/^{\circ}\text{K}$	$10^{-5}/^{\circ}\text{K}$	$10^{-7}/(^{\circ}\text{K})^2$	$10^{-7}/(^{\circ}\text{K})^2$
LiF	26.96	243.6	- 4.44	0.90	8.1
NaF	28.25	143.3	- 5.81	2.00	10.2
NaCl	31.59	186.2	-11.29	2.28	13.5
NaBr	32.78	209.7	-13.22	2.38	15.2
KCl	29.48	141.8	-10.67	2.77	13.4
KBr	29.82	145.3	-12.28	2.79	13.6

TABLE X. Literature Values of the Temperature Derivatives of the SDC.

	[66] $\frac{1}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial T} \right)_p$ Lowndes	[67] [70] $\frac{1}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial T} \right)_p$ Havinga	[71] $\frac{1}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial T} \right)_p$ Robinson
Units	$10^{-5}/^{\circ}\text{K}$	$10^{-5}/^{\circ}\text{K}$	$10^{-5}/^{\circ}\text{K}$
LiF	28.2	37.3	—
NaF	30.0	—	—
NaCl	31.7	32.4	32.1
NaBr	33.4	—	—
KCl	28.8	29.5	29.3
KBr	30.7	31.7	31.0

DISCUSSION

A. The Static Dielectric Constant

It is useful to begin a discussion of the SDC by considering polarizability concepts. To this end, it is convenient to calculate polarizabilities referred to molecular volumes. This is achieved by defining:

$$\alpha = N''\alpha_m \quad (81a)$$

and

$$\alpha_e = N''\alpha_e^m \quad (81b)$$

where N'' is the number of ion pairs per fictitious sphere, and by substituting these equations into Eqs. (19) and (21) respectively. Realizing that:

$$NN'' = N' \quad (82)$$

we may calculate the molecular volume polarizabilities using the basic data listed in Table I. The results of these calculations are listed in Table XI.

The last four samples permit a test of additivity for both frequency ranges:

$$(\alpha_m)_{\text{NaCl}} + (\alpha_m)_{\text{KBr}} = 16.31$$

and

$$(\alpha_m)_{\text{NaBr}} + (\alpha_m)_{\text{KCl}} = 16.52,$$

TABLE XI. Various aspects of the polarizability of the alkali halides being investigated.

	α_m	α_e^m	Electronic Contribution	$(\alpha_e^+)_a$	$(\alpha_e^+)_{\text{free}}^{[46]}$	$(\alpha_e^-)_a$	$(\alpha_a^-)_{\text{free}}^{[46]}$
Units	10^{-24} cm^3	10^{-24} cm^3	%	10^{-24} cm^3	10^{-24} cm^3	10^{-24} cm^3	10^{-24} cm^3
LiF	2.838	.919	32	.075	.075	.844	.99
NaF	3.421	1.178	34	.334	.21	.844	.99
NaCl	6.640	3.288	50	.334	.21	2.954	3.05
NaBr	8.192	4.434	54	.334	.21	4.110	4.17
KCl	8.326	4.182	50	1.228	.87	2.954	3.05
KBr	9.672	5.348	55	1.228	.87	4.110	4.17

for the low frequencies, and:

$$(\alpha_e^m)_{\text{NaCl}} + (\alpha_e^m)_{\text{KBr}} = 8.636$$

and

$$(\alpha_e^m)_{\text{NaBr}} + (\alpha_e^m)_{\text{KCl}} = 8.616$$

for high frequencies.⁴² The results tend to confirm the assertion that the Lorentz-Lorenz equation has more applicability in describing dielectric phenomena than does the Clausius-Mossotti equation. It has, in fact, a microscopic extension as pointed out in Eq. (23). Making the identification:

$$(\alpha_e^m) = (\alpha_e^+)_{\text{a}} + (\alpha_e^-)_{\text{a}} \quad (83)$$

we calculate the electronic polarizabilities of ions in crystals by fixing $(\alpha_e^+)_{\text{a}}$ for lithium from the tables of Born and Heisenberg⁴⁶ and the rest of the values were calculated assuming additivity. A unique sequence for all but NaBr was followed, and the value listed for that crystal is the average of the two resultant calculations. The results are given in Table VI along with the "free" ion values of Born and Heisenberg. It is seen that the values determined by this procedure are larger for the positive ions and smaller for the negative ions than the "free" ion values. A partial explanation of this effect can be formulated using the mechanical repulsion of the shell model. If the ions have different polarizabilities, there will be different amounts of quantum mechanical repulsion at the two "different" contact points. This

would produce an effective repulsion between the shells at the contact point of greater overlap. In the case of the above samples, this effect is of the right sign in that the negative ion has the greater polarizability.

It is probably true, however, that this mechanism is only partially responsible for the difference between the polarizabilities of free ions and ions in crystals, and that calculations of the total effect will come from the quantum theory of solids. Ledovskaya⁴⁷ has made a significant advance toward this end obtaining results in qualitative agreement with the above observations. Mitskevich⁴⁸ and Heinrichs⁴⁹ have also made relevant contributions.

As has already been pointed out, the Clausius-Mossotti formula has no microscopic significance when applied to ionic crystals, and, thus, it is necessary to revert to more complex models to describe the total SDC. The first such model worth consideration is the simple Born model. The predictions of this model for the SDC based on the best data available are listed in Table I where they are compared with the experimental results of this work. In most cases, the predictions are better than originally thought by Born, however, it is obvious that this model does not adequately describe the SDC of an ionic crystal, the predictions ranging from 4-15% lower than the experimentally observed values.

The results of Szigeti's^{17,18} first modification of the Born theory are shown in Table XII which shows the necessity for

TABLE XII. Considerations related to the effective charge.

	(ϵ_s) Modified Born	e^*/e (Obs)	(e^*/e) [19] D & O	(e^*/e) [19] D & O extreme	(e^*/e) [20] H & L	(e^*/e) [28] Mit.
LiF	12.914	.807	.91	.88	.872	.80
NaF	6.608	.827	.93	.86	.916	.85
NaCl	8.417	.765	.91	.84	(.765)	.78
NaBr	9.291	.753	.89	.82	.695	—
KCl	6.196	.810	.93	.84	.849	.83
KBr	6.528	.776	.93	.84	.781	—

the introduction of a proportionality factor, s . The consequential effective charges calculated from Eq. (25) are also listed in Table XII. These are the best values to date by virtue of the 0.01% experimental SDC. The quantity e^*/e , however, is limited to an accuracy of about a percent by the 0.5% values of v_t . This confidence level, though, permits a rather close evaluation of the more sophisticated models. The next picture in the sequence presented in the "Theory" section is the exchange charge model of Dick and Overhauser.¹⁹ Values of e^*/e calculated on the basis of their model, Eq. (26), are listed in columns 4 and 5 of Table XII. The quantity $(e^*/e)_{D\&O}$ is calculated with the exchange charge at the ion-ion contact points while $(e^*/e)_{\text{extreme}}$ is evaluated for the extreme case of the exchange charge placed at the positive ion core. Comparison of these values to the experimental results shows that while the magnitudes of the normal calculations are different from the observed values, they represent the relative change in e^*/e with the variation of the cation and/or anion species rather well. Another observation is that while the magnitudes of $(e^*/e)_{\text{extreme}}$ are closer to the observed values, they tend to obscure the variation of e^*/e with cation and anion. Since the normal calculation contains a slightly greater contribution from mechanical repulsion, it appears that this physically plausible mechanism is at least partially responsible for the reduction of the effective charge from one. The smearing effect of moving the exchange charge to the nucleus comes as little surprise in that it

deviates from the physics of the situation. The idea of the addition of a neutralization charge, however, remains as an interesting device for simulating the effects of the quantum mechanical charge redistribution.

There are also some comments that can be made regarding the model of Hanlon and Lawson²⁰ by virtue of the accuracy of the present results. The motivation for their work was the observation that a plot of the effective charge versus the difference in the polarizabilities of the positive and negative ions showed that a functional relationship existed for many alkali halides. A similar plot is made in Figure 6 based on the values of e^*/e from this work and the polarizabilities from a newly refined table.¹¹ It is seen there that there is no single relationship between the points, but, rather, internal structure is evident. Thus, it is possible that the Hanlon and Lawson model could account for the individual families of curves. This was tested by using the experimental value of e^*/e for NaCl in Eq. (27) to find a value of f . This value of f was then used in Eq. (27) to predict the values of e^*/e listed in column 6 of Table XII. It is seen there that the predictions are not very accurate. This is not very surprising in that the model itself is probably incomplete containing only the effects of mechanical repulsion. It is also noted that the relative variation of e^*/e is fairly well accounted for which is consistent with the observations for the "normal" exchange charge model.

FIGURE 6. Plot of the Szigeti Effective Charge Versus the Difference in Polarizability Between the Positive and Negative Ions. e^*/e for KF Was Taken from Lowndes and Martin⁴² While the Polarizabilities were Obtained from Pirenne and Kartheuser.¹⁰

The other model mentioned in the "Theory" section is the deformation dipole model of Hardy.^{25,26} This is a phenomenological model in which the resultant induced dipoles are lumped into the "distortion" dipole. To describe this distortion dipole, Hardy generalized the exchange charge expression of Dick and Overhauser. He then plotted the observed values of $(1-e^*/e)$ versus the approximate expression:

$$10^{21} \times \lambda (r_-^2 - r_+^2) (1/\rho'' - 2/R_0) \exp(-R_0/\rho'') \quad (84)$$

which is derived from Eq. (30) making the assumptions that $d=d^+=d^-$, a constant. Hardy found that the rubidium and potassium salts were on a straight line through the origin consistent with his theory, and that the sodium salts were on another straight line. He goes on to make an argument that brings the lines into coincidence. A new plot of $(1-e^*/e)$ using the experimental values of e^*/e from this work and elsewhere⁴² versus Hardy's abscissa is shown in Figure 7. Again, a family of curves is observed, none of which appear to go through the origin. It then appears that a major revision of the existing treatment of the deformation dipole model is needed.

On the basis of the internal structure revealed when e^*/e is plotted versus parameters intrinsic to ionic crystals, both those plots seen here and elsewhere,⁴² it seems highly improbable that a simple, useful, self-consistent phenomenological theory of the SDC will be achieved. It seems necessary, then, to revert to more

FIGURE 7. Test of the Deformation Dipole Theory of Hardy.^{25,26} e^*/e for the Rubidium Compounds KI, and NaI are Taken from Lowndes and Martin.⁴²

sophisticated theories of the SDC. In this regard, Brown⁵⁶ has pointed out that a complete description of dielectrics involves the simultaneous consideration of quantum theory, statistical mechanics, and many-body considerations.³⁰

At the present time, useful quantitative results have been obtained in only one of these areas, quantum mechanics. One of the first workers to obtain numerical results was Yamashita.²⁹ He used a variational method, and evaluated exchange integrals to arrive at the dielectric constant for LiF. The results are listed in Table XIII, and are seen to compare favorably with the observed values considering the large number of approximations that must be made in such a calculation. The value quoted for his value of ϵ^*/ϵ is the number obtained by Levin and Offenbacher³⁰ from Yamashita's data in that they noted a mistake in one of his final steps. Levin and Offenbacher also made calculations of their own following the general procedure of Yamashita but including new energy considerations, and using both orthogonal and nonorthogonal wave functions. Their results for the SDC of LiF are in about the same agreement with the experimentally observed values as Yamashita's, but a significant improvement in the values of ϵ^*/ϵ is noted. Finally, the values of n^2 calculated by Levin and Offenbacher show that orthogonalized wave functions should be used in future quantum mechanical calculations of the SDC.

Mitskevich²⁸ also has used quantum mechanical methods to determine the effective charge for some alkali halides. His results

TABLE XIII. Quantum theoretical calculation of ϵ_s , n^2 and e^*/e for LiF

	ϵ_s	n^2	e^*/e
Yamashita	10.1	2.33	1.06
Nonorthogonal wave function Levin & Offenbacher	8.0	2.63	.79
Orthogonal wave function Levin and Offenbacher	8.1	1.59	.88
Observed	9.0357	1.926	.807

are listed in the last column of Table XII, and it is seen that the results are in good agreement with the experimental data.

The results for the SDC have been discussed in the light of room temperature experimental results for the sakes of both internal consistency and conformity with the literature. Most of the models should be evaluated at 0°K however. The important 0°K parameters have been determined using temperature extrapolations of the SDC of this work and necessary literature data. The results are listed in Table XIV, and the numbers merely punctuate the conclusions drawn above.

B. The Pressure and Temperature Derivatives of the SDC

As in the treatment of the SDC itself, the starting point for discussing the pressure and temperature derivatives of the SDC is to consider the implications of the Clausius-Mossotti equation. The temperature and pressure derivatives of the polarizability were determined from Eqs. (44) and (47) respectively, and are listed in Table XV. In addition, the pressure derivative of the electronic polarizability⁵³ is listed, and was obtained from the high frequency analogy to Eq. (47) where the substitutions $\alpha \rightarrow \alpha_e$ and $\epsilon_s \rightarrow n^2$ have been made. The consequences of Eq. (47) are listed in Table XVI, and it is interesting to note that the negative contribution from the decrease in polarizability as pressure increases is about twice as large as the positive contribution from the fact that the number of polarizable particles per unit volume increases. The

TABLE XIV. 0°K Basic Data and the Szigeti Effective Charge.

	ϵ_s	n^2 [42]	N^1	ν_t [42]	(e^*/e)	$(\epsilon_s)_{\text{Born}}$
Units	—	—	$10^{22}/\text{cm}^3$	$\times 10^{12}/\text{sec}$	—	—
LiF	8.3229	1.933	6.2260	9.534	.790	7.893
NaF	4.6812	1.751	4.0904	7.855	.815	4.570
NaCl	5.3866	2.351	2.2860	5.336	.753	4.897
NaBr	5.8248	2.640	1.9260	4.377	.731	5.131
KCl	4.4398	2.204	1.6436	4.527	.773	4.112
KBr	4.4943	2.390	1.4288	3.688	.745	4.160

TABLE XV. Pressure and Temperature Derivatives of the Polarizability.

	$\frac{1}{\alpha} \left(\frac{\partial \alpha}{\partial p} \right)_T$	$\frac{1}{\alpha_e} \left(\frac{\partial \alpha_e}{\partial p} \right)_T$	$\frac{1}{\alpha} \left(\frac{\partial^2 \alpha}{\partial p^2} \right)_T$	$\frac{1}{\alpha} \left(\frac{\partial \alpha}{\partial T} \right)_p$	$\frac{1}{\alpha} \left(\frac{\partial^2 \alpha}{\partial T^2} \right)_p$
Units	$10^{-12} \left(\frac{\text{cm}^2}{\text{dy}} \right)$	$10^{-12} \left(\frac{\text{cm}^2}{\text{dy}} \right)$	$10^{-24} \left(\frac{\text{cm}^2}{\text{dy}} \right)^2$	$10^{-5}/^\circ\text{K}$	$10^{-7}/(^\circ\text{K})^2$
LiF	- 3.090	-1.082	32.20	18.59	1.66
NaF	- 5.018	-1.390	84.02	24.84	2.08
NaCl	- 8.985	-2.369	308.90	26.53	1.65
NaBr	-10.507	-3.062	459.00	26.63	1.43
KCl	-11.949	-2.549	577.60	27.58	1.92
KBr	-13.694	-3.042	811.60	28.16	2.01

TABLE XVI. Contributions to the First Pressure Derivatives of the Total and Electronic Dielectric Constants.

Units $10^{-12} \left(\frac{\text{cm}^2}{\text{dy}} \right)$	$\frac{3}{(\epsilon_s - 1)(\epsilon_s + 2)} \left(\frac{\partial \epsilon_s}{\partial p} \right)_T = \chi_T + \frac{1}{\alpha} \left(\frac{\partial \alpha}{\partial p} \right)_T$			$\frac{3}{(n^2 - 1)(n^2 + 2)} \left(\frac{\partial n^2}{\partial p} \right)_T = \chi_T + \frac{1}{\alpha_e} \left(\frac{\partial \alpha_e}{\partial p} \right)_T$		
LiF	-1.544	1.536	- 3.090	.454	1.536	-1.082
NaF	-2.852	2.166	- 5.018	.776	2.166	-1.390
NaCl	-4.754	4.231	- 8.985	1.862	4.231	-2.369
NaBr	-5.380	5.127	-10.507	2.065	5.127	-3.062
KCl	-6.119	5.830	-11.949	3.281	5.830	-2.549
KBr	-6.857	6.837	-13.694	3.795	6.837	-3.042

situation is just reversed for high frequencies where the increase due to the change in the number of ions per unit volume is about twice as large as the decrease in polarizability.

Similar observations are made for the contributions to the temperature derivatives which are calculated using Eq. (44) and tabulated in Table XVII. It is noted that the increase of polarizability with temperature dominates the purely particle density effect by a factor of two. Reliable data for the change of refractive index with temperature is not available, and, thus, comparison with purely electronic effects will not be made.

The various first derivatives of the polarizability can be separated further using Eqs. (46), (49), (51), and (52). The results are listed in Table XVIII. The physically meaningful derivatives are $v(\partial\alpha/\partial v)_T$ and $(\partial\alpha/\partial T)_v$ and their relative contributions to $(\partial\alpha/\partial T)_p$ are shown in Table XVII. The temperature independent quantity displays a purely volume dependent effect on the polarizability, and it is seen that the polarizability decreases with volume.

The volume independent derivative shows seemingly anomalous results in that five of the six crystals show positive values for $(\partial\alpha/\partial T)_v$ while LiF has a negative value. Since the volume dependent effect is directly related to the same derivative of the SDC by the relation:

$$\left(\frac{\partial\alpha}{\partial T}\right)_v = \frac{3}{(\epsilon_s - 1)(\epsilon_s + 2)} \left(\frac{\partial\epsilon}{\partial T}\right)_v \quad (85)$$

TABLE XVII. Contributions to the Experimental First Temperature Derivative of the SDC and to the quantity $1/\alpha(\partial\alpha/\partial T)_p$.

Units $10^{-5}/^{\circ}\text{K}$	$\frac{3}{(\epsilon_s-1)(\epsilon_s+2)} \left(\frac{\partial\epsilon_s}{\partial T}\right)_p = \frac{1}{\alpha} \left(\frac{\partial\alpha}{\partial T}\right)_p - \gamma_p$			$\frac{1}{\alpha} \left(\frac{\partial\alpha}{\partial T}\right)_p = \frac{1}{\alpha} \left(\frac{\partial\alpha}{\partial T}\right)_V + \frac{V\gamma_p}{\alpha} \left(\frac{\partial\alpha}{\partial V}\right)_T$		
LiF	8.24	18.59	10.35	18.59	-2.23	20.82
NaF	14.92	24.85	9.925	24.85	1.85	23.00
NaCl	14.46	26.53	12.075	26.53	0.89	25.64
NaBr	13.88	26.63	12.75	26.63	0.50	26.13
KCl	16.39	27.58	11.19	27.58	4.64	22.93
KBr	16.37	28.16	11.79	28.16	4.54	23.62

TABLE XVIII. Various Thermodynamic Derivatives of the Polarizability of Some Alkali Halides.

	$\frac{1}{\alpha} \left(\frac{\partial \alpha}{\partial T} \right)_v$	$\frac{v}{\alpha} \left(\frac{\partial \alpha}{\partial v} \right)_T$	$\frac{v^2}{\alpha} \left(\frac{\partial^2 \alpha}{\partial v^2} \right)_T$	$\frac{1}{\alpha} \left(\frac{\partial \alpha}{\partial p} \right)_v$	$\frac{v}{\alpha} \left(\frac{\partial \alpha}{\partial v} \right)_p$	$\frac{v^2}{\alpha} \left(\frac{\partial^2 \alpha}{\partial v^2} \right)_p$
Units	$10^{-5}/^\circ\text{K}$	—	—	$10^{-12} \frac{\text{cm}^2}{\text{cy}}$	—	—
LiF	-2.233	2.011	1.80	- .331	1.796	-10.96
NaF	1.854	2.317	3.13	.404	2.504	-12.67
NaCl	.891	2.123	3.30	.312	2.197	-2.85
NaBr	.501	2.049	4.68	.201	2.088	-1.00
KCl	4.642	2.049	3.90	2.419	2.464	1.65
KBr	4.546	2.003	4.41	2.636	2.388	.96

the discussion of this effect will be given later. It is also seen in Table XVII that the volume dependent contribution to the variation of polarizability with temperature is from five to fifty times greater than the purely temperature effect.

In addition, the curvatures of the above quantities were obtained using Eqs. (53), (54), and the polarizability analogies to Eqs. (41), and (43). The results of these calculations are also listed in Tables XV and XVIII. As would be expected for materials which become increasingly less responsive as the lattice constant is decreased, the experimental second derivatives are all positive. The second pressure derivatives increase monotonically with increasing cation and/or anion radius, but the sodium series temperature derivatives exhibit the opposite effect.

Again it is noted that the implications of the Clausius-Mossotti formulation are of a macroscopic nature. In discussing the SDC from an atomistic point of view, it is convenient to treat the volume dependent and volume independent effects separately.

1. The Volume Dependent Effect

The first order volume dependent contribution to the total temperature variation of the SDC was calculated using Eq. (34) and the data from Tables V and VI. The results are listed in Table XIX. The predictions of the simple Born model for $v(\partial\epsilon/\partial v)_T$ were calculated using Eq. (55), and the results tabulated in Table II are seen to agree fairly well with experiment. We know, however,

TABLE XIX. First Order Volume Derivatives of the SDC of Some Alkali Halides.

	$\left(\frac{\partial \epsilon_s}{\partial p}\right)_v$	$v\left(\frac{\partial \epsilon_s}{\partial v}\right)_p$	$\left(\frac{\partial \epsilon_s}{\partial T}\right)_v$	$v\left(\frac{\partial \epsilon_s}{\partial v}\right)_T$
Units	$10^{-12} \left(\frac{\text{cm}^2}{\text{dy}}\right)$	—	$10^{-5}/^\circ\text{K}$	—
LiF	-9.80	23.54	-66.02	29.91
NaF	3.88	14.44	17.80	12.64
NaCl	4.02	15.42	11.48	14.47
NaBr	3.05	16.44	7.58	15.85
KCl	20.93	12.67	40.19	9.08
KBr	23.40	12.33	40.36	8.90

that important effects have been omitted from this picture. Including the long range interaction of the transverse waves with the ions and using Eq. (27), we evaluate the change of overlap with volume. The results are listed in Table XX along with the maximum possible error when the quantity $x_T(2\gamma_{T0}-1)$ is assigned an uncertainty of 20%. It is seen that five of the six values are positive, three of which are almost certainly so. The results indicate a definite trend toward positive values for $(\partial e^*/\partial v)_T$ which is consistent with the physics that the effective charge should decrease as the volume decreases. This result is, however, in disagreement with the calculations of Barron³³ based on the dielectric constant data of Jones.⁶⁵ It should be noted, however, that Barron's work utilizes a theoretical value of γ_{T0} , and that the results are primarily limited by the accuracy of this quantity. Measurements of γ_{T0} have been undertaken only recently with the first values appearing in 1967.⁵⁰ The values quoted in this work are the numerical averages of all the numbers available⁵⁰⁻⁵² for a given crystal including a value for NaF obtained from longitudinal optical measurements on that crystal which were transformed to γ_{T0} using the volume derivative of the Lyddane, Sachs, Teller¹⁶ relation:

$$\frac{\epsilon_s}{n^2} = \frac{v_1^2}{v_t^2} \quad (86)$$

which is:

TABLE XX.

Calculations Related to the Volume Variation of the Szigeti Effective Charge and Longitudinal Optic Grüneisen Parameters.

	$\frac{v}{e^*} \left(\frac{\partial e^*}{\partial v} \right)_T$ obs	γ_{LO}	$\frac{v}{e^*} \left(\frac{\partial e^*}{\partial v} \right)$ D&O	$\frac{v}{e^*} \left(\frac{\partial e^*}{\partial v} \right)$ D&O Extreme	$\frac{v}{e^*} \left(\frac{\partial e^*}{\partial v} \right)$ phenon	$\frac{v}{e^*} \left(\frac{\partial e^*}{\partial v} \right)$ Hardy	$\frac{v}{e^*} \left(\frac{\partial e^*}{\partial v} \right)$ Mit
LiF	.57 ± .4	.40 ± .4	.021	.067	.36	1.56	1.37
NaF	.14 ± .4	1.05 ± .5	.032	.23	.42	1.38	1.45
NaCl	.74 ± .4	.69 ± .4	.079	.29	.71	2.61	2.42
NaBr	1.68 ± .2	-.17 ± .4	.096	.32	.80	2.90	—
KCl	-.06 ± .4	1.52 ± .5	.050	.37	.62	2.20	1.92
KBr	.02 ± .4	1.57 ± .5	.066	.38	.78	2.76	—

$$\gamma_{TO} - \gamma_{LO} = \frac{v}{2\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial v} \right)_T - \frac{v}{n} \left(\frac{\partial n}{\partial v} \right)_T \quad (87)$$

where:

$$\gamma_{TO} = - \frac{v}{v_l} \left(\frac{\partial v_l}{\partial v} \right)_T \quad (88)$$

is the long wavelength longitudinal optical Gruneisen parameter.

As a sidelight of this work, longitudinal optical Gruneisen parameters were calculated using Eq. (87) and the necessary data from this work, and are listed in Table XX. Again, the results are limited by the accuracy of γ_{TO} .

The quantity $v/e^*(\partial e^*/\partial v)_T$ can be evaluated theoretically. The first calculation that we consider is based on the model of Dick and Overhauser¹⁹ as formulated by Fuchs.³² Purely theoretical predictions were made by substituting the theoretical values for D/e and $(D/e)_{\text{extreme}}$ from the paper by Dick and Overhauser into Eq. (58) along with the Born model parameters R_0 and p'' from the tables by Tosi.⁷² In addition, a phenomenological calculation was made on the basis of Fuchs' assertion that:

$$D/e = e^*/e - 1 \quad (89)$$

using our values for e^*/e . The results of all three calculations are listed in Table XX. It is noted that this model predicts positive values which is in agreement with experiment. Also, it appears that the order of magnitude agreement between the values

calculated from $(D/e)_{\text{extreme}}$, (e^*/e) , and the observed values is consistent with the model predictions for e^*/e . This again suggests that it may be worthwhile to reevaluate the exchange charge concepts, namely calculation of the quantity D/e .

Next, the predictions of the deformation dipole models of Hardy^{25,26} and Mitskevich²⁸ as set down by Barron³³ were obtained using Eq. (59). The input parameters were taken from the tables by Tosi⁷² for Hardy's model while Mitskevich²⁸ has supplied his own. The results are also tabulated in Table XX. The predictions of these models are again positive and agree fairly well with each other. They predict larger values than does the exchange charge model, however, due to the uncertainty in the observed values of $(\partial e^*/\partial v)_T$, nothing further can be said about these predictions.

Finally, we mention Yamashita's³⁴ quantum mechanical of the temperature independent volume derivative of the SDC for LiF. Yamashita arrives at the value:

$$\frac{v}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial v} \right)_T \gamma_p = 4.5 \times 10^{-4}/^\circ\text{K}$$

which is to be compared with our result:

$$\frac{v}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial v} \right)_T \gamma_p = 3.43 \times 10^{-4}/^\circ\text{K}$$

The values agree fairly well considering the number of approximations that need to be made in such a quantum mechanical calculation.

Listed in Table XXI are the various second order derivatives

TABLE XXI. Second Order Volume Derivatives of the SDC of Some Alkali Halides.

	$\left(\frac{\partial^2 \epsilon_s}{\partial p^2} \right)_v$	$v^2 \left(\frac{\partial^2 \epsilon_s}{\partial v^2} \right)_p$	$\left(\frac{\partial^2 \epsilon_s}{\partial T^2} \right)_v$	$v^2 \left(\frac{\partial^2 \epsilon_s}{\partial v^2} \right)_T$
Units	$10^{-24} \left(\frac{\text{cm}^2}{\text{dy}} \right)^2$	—	$10^{-7} / (^{\circ}\text{K})^2$	—
LiF	(562.1)	-270.73	(35.16)	155.7
NaF	(667.8)	- 91.51	(15.15)	50.0
NaCl	(4084.5)	- 7.34	(39.01)	66.7
NaBr	(8254.5)	16.38	(50.93)	98.9
KCl	(8266.4)	36.15	(29.08)	39.8
KBr	(10312.2)	28.09	(29.48)	44.4

of the SDC calculated from Eqs. (40)-(43). The second and fourth columns are in parentheses because they were calculated omitting the cross derivative ($\partial^2 \epsilon_s / \partial p \partial T$). This term has been shown by Lowndes and Martin⁶⁶ to be positive, and, thus, the values in columns 2 and 4 of Table XXI should be slightly more positive. It is noted that the second order temperature independent volume derivative is positive in every case as would be expected on physical grounds.

2. The Volume Independent Effect

The volume independent variation of the SDC, however, does not lend itself to a straightforward interpretation. This is particularly apparent in examining the $(\partial \epsilon_s / \partial T)_V$ in Table XIX or in Table XXII where its experimental constitution via Eq. (36) is given. It is seen that the value for LiF is negative while all of the other crystals show positive values. This is thought to be real in that ascribing an uncertainty of 0.5% to the pressure derivative, 1% to the thermal expansion coefficient, and 0.5% to the temperature derivative, the maximum value obtainable for $(\partial \epsilon_s / \partial T)_V$ is -40×10^{-5} . This result is not particularly surprising in the light of other dielectric constant data⁷⁰ for it has been known for several years that $(\partial \epsilon_s / \partial T)_V < 0$ for $\epsilon_s > 10$ and $(\partial \epsilon_s / \partial T)_V > 0$ for $\epsilon_s < 10$. This work suggests a lowering of the cut off. A test of this hypothesis will be to obtain accurate values of $(\partial \epsilon_s / \partial T)_V$ for MgO which shows a value of around 9.8 for ϵ_s . One

TABLE XXII. Thermodynamic Separation of the Temperature Derivatives of the SDC.

Units $10^{-5}/^{\circ}\text{K}$	$\left(\frac{\partial \epsilon_s}{\partial T}\right)_v = \left(\frac{\partial \epsilon_s}{\partial T}\right)_p + \frac{\gamma_p}{\chi_T} \left(\frac{\partial \epsilon_s}{\partial p}\right)_T$		
LiF	-66.0	243.6	-309.6
NaF	17.8	143.3	-125.5
NaCl	11.4	186.2	-147.8
NaBr	7.6	209.7	-202.1
KCl	40.1	141.8	-101.7
KBr	40.3	145.3	-105.0

worker⁶⁹ quotes a negative value of $(\partial\epsilon_s/\partial T)_V$ for this crystal while others^{70,73} say it is positive. As pointed out in the "Theory" section, the position of the cut off will be important to theoreticians when they are able to calculate the quantities on the right hand side of Eq. (65). It is also interesting to note that Yamashita's³⁴ quantum theoretical calculation of $(\partial\epsilon_s/\partial T)_V$ for LiF:

$$\frac{1}{\epsilon_s} \left(\frac{\partial\epsilon_s}{\partial T} \right)_V = -1.3 \times 10^{-4}/^\circ\text{K}$$

is also negative in agreement with our value:

$$\frac{1}{\epsilon_s} \left(\frac{\partial\epsilon_s}{\partial T} \right)_V = -.74 \times 10^{-4}/^\circ\text{K}$$

As pointed out in the "Theory" section, quantitative treatments of positive values of $(\partial\epsilon_s/\partial T)_V$ are absent at the present time while calculations able to predict negative values are in a rather primitive state. There is use for $(\partial\epsilon_s/\partial T)_V$, however, in that it may be used to calculate the anharmonic contribution to the lattice segment of the SDC via Eq. (73) and, thus, the applicability of quasi-harmonic approximation in describing dielectric phenomena may be evaluated anyway. The results of the calculation of the quantity G are listed in Table XXIII. It is noted that the anharmonic contribution varies from about -3% to +5%. This shows that the quasi-harmonic approximation, while unable to account for some lattice thermal effects probably is capable of describing the thermal variation of the SDC fairly well.

TABLE XXIII. The Anharmonic Contribution
to the Lattice Dielectric
Constant.

	G	$\frac{G}{\epsilon_s - n^2} \times 100\%$
LiF	-.201	-2.8
NaF	.063	1.89
NaCl	.039	1.09
NaBr	.025	.66
KCl	.125	4.74
KBr	.122	4.85

Finally, it is noted in Table XXI that the second derivative for the volume independent effect is always positive.

CONCLUSIONS

By establishing highly accurate values for the SDC of some widely studied alkali halides, this work has shown that existing classical and semiclassical theories of the SDC are more inadequate than heretofore thought. Furthermore, it appears that to obtain a complete microscopic understanding of the SDC of ionic crystals on the basis of such physically understandable theories will be extremely difficult, indeed.

Such general conclusions cannot be drawn from the pressure and temperature derivatives due to the uncertainty inherent in the auxiliary data. However, specific contributions have been made in that for the first time positive values are predicted experimentally for the temperature independent volume derivative of the Szigeti effective charge, and a new cut off is predicted for negative values of the volume independent temperature derivatives of the SDC.

The results, then, should figure prominently in future considerations of the SDC of ionic crystals.

REFERENCES

1. H. A. Lorentz, Theory of Electrons, (Dover Publications Inc., New York, N. Y., 1952), p. 137.
2. C. Kittel, Introduction to Solid State Physics, (John Wiley and Sons, Inc., New York, N. Y. 1956), 2nd. ed.
3. H. Frohlich, Theory of Dielectrics, (Oxford University Press, London, England, 1958), 2nd. ed.
4. B. R. A. Nijboer and F. W. DeWette, Physica, 24, 422, (1958).
5. G. Jaffe, J. Chem. Phys. 8, 879, (1940).
6. W. B. Fowler, Phys. Rev. 151, 657, (1966).
7. R. P. Mercier, Physica 45, 95, (1969).
8. J. Heinrichs, Phys. Letters 18, 251, (1965).
9. J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. 92, 890, (1953).
10. J. Pirene and E. Kartheuser, Physica 30, 2005, (1964).
11. K. G. Aggarwal and B. Szigeti, J. Phys. C. (Solid St. Phys.) 3, 1097, (1970).
12. M. Born and M. Goppert Mayer, Handb. Physik 24, 638, (1933).
13. G. Heckmann, Z. Krist. 61, 250, (1925).
14. A. Eucken and A. Buchner, Z. Physik. Chem. B 27, 321, (1934).
15. N. F. Mott and M. J. Littleton, Trans. Far. Soc. 34, 485, (1938).
16. R. H. Lyddane, R. H. Sachs, and E. Teller, Phys. Rev. 59, 673, (1941).
17. B. Szigeti, Trans. Far. Soc. 45, 155, (1949).
18. B. Szigeti, Proc. Roy. Soc. 204, 51, (1951).
19. B. G. Dick and A. W. Overhauser, Phys. Rev. 112, 90, (1958).
20. J. E. Hanlon and A. W. Lawson, Phys. Rev. 113, 472, (1959).

21. R. A. Cowley, Proc. Roy. Soc. (Lond.) 268, 109, (1962).
22. W. Cochran, Advan. Phys. 9, 387, (1960).
23. S. K. Sinha, Phys. Rev. 177, 1256, (1969).
24. M. Born and K. Huang, Dynamical Theory of Crystal Lattices, (Oxford University Press, London, England, 1954).
25. J. R. Hardy, Phil. Mag. 4, 1278, (1959).
26. J. R. Hardy, Phil. Mag. 6, 27, (1961).
27. S. O. Lundqvist, Arkiv For Fysik 9, 435, (1955).
28. V. V. Mitskevich, Sov. Phys.-Solid State, 5, 2568, (1964).
29. J. Yamashita, Prog. Theoret. Phys. (Kyoto) 8, 280, (1952).
30. E. R. Levin and E. L. Offenbacher, Phys. Rev. 118, 1142, (1960).
31. E. E. Havinga, J. Phys. Chem. Solids 18, 253, (1961).
32. R. Fuchs, Technical Report No. 167, Laboratory for Insulation Research, Massachusetts Institute of Technology.
33. T. H. K. Barron and A. Batana, Phil. Mag. 20, 619, (1969).
34. J. Yamashita, Progr. Theoret. Phys. (Kyoto), 12, 454, (1954).
35. F. C. Frank, Trans. Far. Soc. 42, 250, (1946).
36. J. C. Slater, Phys. Rev. 78, 748, (1950).
37. B. Szigeti, Proc. Roy. Soc. (London) 258, 377, (1960).
38. B. Szigeti, Proc. Roy. Soc. (London) 252, 217, (1959).
39. B. Szigeti, Proc. Roy. Soc. (London) 261, 274, (1961).
40. D. Miliotis and D. N. Yoon, J. Phys. Chem. Solids, 30, 1241, (1969).
41. D. F. Gibbs and B. W. Jones, J. Phys. C (Solid St. Phys.), 2, 1392, (1969).
42. R. P. Lowndes and D. H. Martin, Proc. Roy. Soc. (London) 308, 473, (1969).

43. National Bureau of Standards Circular 539: LiF, NaF, KCl, and KBr, 1, (1953); NaCl, 2, (1953); and NaBr, 3, (1954).
44. The values for LiF, NaF, and NaCl were taken from Reference 42, and the numbers for NaBr, KCl, and KBr are an arithmetical average of the 0.5% data of Reference 42 and G. O. Jones, D. H. Martin, P. A. Mawer, and C. H. Perry, Proc. Roy. Soc. (London), 261, 10, (1961).
45. Handbook of Chemistry and Physics, (The Chemical Rubber Co., Cleveland, Ohio, 1968-69), Forty-Ninth Ed.
46. M. Born and W. Heisenberg, Z. Physik 23, 388, (1924).
47. E. M. Ledovskaya, Phys. Stat. Sol. 31, 507, (1969).
48. V. V. Mitskevich, Sov. Phys.-Solid State 6, 557, (1964).
49. J. Heinrichs, Phys. Rev. B 2, 518, (1970).
50. S. S. Mitra, C. Postmus, and J. R. Ferraro, Phys. Rev. Letters 18, 455, (1967).
51. C. Postmus, J. R. Ferraro, and S. S. Mitra, Phys. Rev. 174, 983, (1968); J. R. Ferraro, C. Postmus, S. S. Mitra, and C. J. Hoskins, Applied Optics 9, 5, (1970).
52. John R. Ferraro, Private Communication.
53. Joseph L. Kirk, Private Communication.
54. This value was obtained by assuming that the fractional change in going from NaCl to NaBr is that same as for KCl to KBr.
55. The values for LiF, NaCl, KCl, and KBr, were taken from Reference 67 while the value for NaBr was obtained by assuming that the fractional change in going from NaCl to NaBr is the same as from KCl to KBr. The value for NaF was obtained by assuming that the fractional change for the pressure derivative for LiF and NaF is the same as for the temperature derivative.
56. W. F. Brown, Encyclopedia of Physics 17, (1956).
57. B. W. James and B. Yates, Phil. Mag. 12, 253, (1965).
58. R. A. Bartels and D. E. Schuele, J. Phys. Chem. Solids 26, 537, (1965).
59. R. W. Roberts and C. S. Smith, J. Phys. Chem. Solids 31, 619, (1970).

60. G. Leibfried and W. Ludwig, Solid State Phys., (eds. F. Seitz and D. Turnbull), 12, 367, Academic Press, New York, (1961).
61. R. A. Miller and C. S. Smith, J. Phys. Chem. Solids 25, 1279, (1964).
62. F. A. Henglein, Z. Electrochem. 31, 424, (1925).
63. B. Yates and C. H. Panter, Proc. Phys. Soc. 80, 373, (1962).
64. K. Loje and D. Schuele, J. Phys. Chem. Solids, In the press.
65. B. W. Jones, Phil. Mag. 16, 1085, (1967).
66. R. P. Lowndes and D. H. Martin, Proc. Roy. Soc. (London) 316, 351, (1970).
67. E. E. Havinga and A. J. Bosman, Phys. Rev. 140, 292, (1965).
68. D. F. Gibbs and M. Jarman, Phil. Mag. 7, 663, (1962).
69. S. Mayburg, Phys. Rev. 79, 375, (1950).
70. A. J. Bosman and E. E. Havinga, Phys. Rev. 129, 1593, (1963).
71. M. C. Robinson and A. C. Hollis Hallett, Can. J. Phys. 44, 2211, (1966).
72. M. Tosi, Solid State Phys., (eds. F. Seitz and D. Turnbull), 16, 1, Academic Press, New York, (1964).
73. G. J. Hill, Nature, 4822, 1275, (1962).
74. C. Andeen, J. Fontanella, and D. Schuele, Rev. Sci. Instr., in the press; AEC Tech. Rep. 63 (COO-623-150).
75. C. Andeen, J. Fontanella, and D. Schuele, Phys. Rev., in the press; AEC Tech. Rep. 66 (COO-623-153).
76. C. Andeen, J. Fontanella and D. Schuele, Submitted to J. Appl. Phys.; AEC Tech. Rep. 67 (COO-623-154).
77. C. Andeen, J. Fontanella, and D. Schuele, Submitted to Rev. Sci. Instr.; AEC Tech. Rep. 68 (COO-623-155).

APPENDIX I

Literature on Dielectric Formlism Applicable to Ionic Crystals Since 1950 Referred to in the Text but not Specifically Cited.

Adler, Stephen L. "Quantum Theory of the Dielectric Constant in Real Solids." Physical Review, April 15, 1962, pp. 413-420.

Abrikosov, A.A.; Gor'kov, L.P.; and Dzyaloshinskiv. Quantum Field Theoretical Methods in Statistical Physics. New York: Pergamon Press, 1965.

Ambegaokar, Vinay, and Kohn Walter. "Electromagnetic Properties of Insulators." Physical Review, January 15, 1960, pp. 423-431.

Askar, A.; Lee, P.C.Y.; and Cakmak, A.S. "Lattice-Dynamics Approach to the Theory of Elastic Dielectric with Polarization Gradient." Physical Review A, April 15, 1970, pp. 3525-3537.

Aspnes, David E. "Electric Field Effects on the Dielectric Constant of Solids." Physical Review, January 15, 1967, pp. 972-982.

Barron, T.H.K. "Long-Wave Optical Vibrations in Simple Ionic Crystals." Physical Review, September 15, 1961, pp. 1995-1998.

Cohen, Morrel H. "Generalized Self-Consistent Field Theory and the Dielectric Formulation of the Many-Body Problem." Physical Review, May 15, 1963, pp. 1301-1309.

Cowley, R.A. "The Elastic and Dielectric Properties of Crystals with Polarizable Atoms." Proceedings of the Royal Society (London) A(GB) June 19, 1962, pp. 121-144.

- Cowley, R.A. "The Lattice Dynamics of an Anharmonic Crystal." Advances in Physics, October 1963, pp. 421-480.
- Cowley, R.S., et al. "Lattice Dynamics of Alkali Halide Crystals. III. Theoretical." Physical Review, August 1, 1963, pp. 1030-1039.
- Dexter, D.L., and Heller, W.R. "Quantum Theory of the Polarizability of an Idealized Crystal." Physical Review, July 15, 1953, pp. 273-278.
- DeWette, F.W. "Effects of Atomic Polarization in Ionic Crystals." Physica, 1959, pp. 1225-1240.
- Dixon, Roy C., and Eringen, A. Cemal. "A Dynamical Theory of Polar Elastic Dielectrics I." International Journal of Engineering Science, August 1965, pp. 359-398.
- Fano, U. "Atomic Theory of Electromagnetic Interactions in Dense Materials." Physical Review, September 1, 1956, pp. 1202-1218.
- Fry, J.L. "Dielectric Function of a Model Insulator." Physical Review, March 15, 1969, pp. 179-905.
- Grindlay, J. "Elastic Dielectric." Physical Review, September 16, 1966, pp. 637-645.
- Hajicek, P. "Equivalence of Toupin's and Grindlay's Theories of Elastic Dielectrics." Physics Letters, July 17, 1967, pp. 36-37.

- Hardy, J.R. "Lattice Dynamics of Alkali Halide Crystals in Relation to Specific Heat Data." Philosophical Magazine, February, 1962, pp. 315-336.
- Heinrichs, Jean. "Theory of the Dielectric Constant in the Individual-Ion Model of Ionic and Rare-Gas Crystals." Physical Review, March 15, 1969, pp. 823-836.
- Hopfield, J.J. "Theory of the Contribution of Excitons to the Complex Dielectric Constant of Crystals." Physical Review, December 1, 1958, pp. 1555-1567.
- Kaneyoshi, Takahito. "Contribution to the Theory of Dielectrics." Progress of Theoretical Physics, March, 1969, pp. 577-585.
- Kittel, C. Quantum Theory of Solids. New York: John Wiley & Sons, Inc., 1963.
- Kohn, W. "Effective Mass Theory in Solids from a Many-Particle Standpoint." Physical Review, January 15, 1957, pp. 509-516.
- Krishnan, K.S., and Roy, S.K. "The Polarization Fields and the Resonance Frequencies of the Alkali Halide Crystals." Philosophical Magazine, January, 1953, pp. 19-32.
- Ledovskaya, E.M. "The Electronic Polarizabilities of Ions in Alkali Halide Crystals." Physica Status Solidi, February, 1969, pp. 507-513.
- Martin, D.H. "The Study of the vibrations of Crystal Lattices by Far Infra-Red Spectroscopy." Advances in Physics, January, 1965, pp. 39-99.

Neufeld, Jacob. "Reformulation of the Dielectric Constant and of Ohm's Law in an Absorbing Medium." Physical Review, December 9, 1966, pp. 708-717.

Nozieres, Philippe, and Pines, David. "Electron Interaction in Solids. Collective Approach to the Dielectric Constant." Physical Review, February 1, 1958, pp. 762-777.

Oitmaa, J. "Dielectric Saturation in Ionic Crystals." Australian Journal of Physics, February, 1967, pp. 11-27.

Pine, Alan S. "Self-Consistent-Field Theory of Linear and Nonlinear Crystalline Dielectrics Including Local-Field Effect." Physical Review, August 2, 1965, pp. A901-911.

Pines, D., and Nozieres, P. The Theory of Quantum Liquids. New York: W.A. Benjamin, Inc., 1966.

Ruffa, A.R. "Theory of the Electronic Polarizabilities of Ions in Crystals: Application to the Alkali Halide Crystals." Physical Review, May 15, 1963, pp. 1412-1423.

APPENDIX II

Relations of the Temperature and Pressure Derivatives of the Static Dielectric Constant to Experimental Observables

The fundamental equation is the expression for the capacitance, C , of a parallel plate capacitor of area A , plate separation d , and dielectric of SDC, ϵ_s :

$$C = \frac{\epsilon_s A}{d} \quad (II.1)$$

Differentiating, then, we obtain:

$$\frac{1}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial p} \right)_T =$$

$$\frac{1}{C} \left(\frac{\partial C}{\partial p} \right)_T + \frac{x_T}{3}$$

(II.2a)

where

$$x_T = - \frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T$$

(II.3a)

Temperature

$$\frac{1}{\epsilon_s} \left(\frac{\partial \epsilon_s}{\partial T} \right)_P =$$

$$\frac{1}{C} \left(\frac{\partial C}{\partial T} \right)_P - \frac{y_P}{3}$$

(II.2b)

where

$$y_P = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

(II.3b)

the isothermal compressibility, the isobaric coefficient of thermal expansion, and,

$$\begin{aligned} \frac{1}{\epsilon_s} \left(\frac{\partial^2 \epsilon_s}{\partial p^2} \right)_T = \\ \frac{1}{C} \left(\frac{\partial^2 C}{\partial p^2} \right)_T + \frac{2\chi_T}{3} \frac{1}{C} \left(\frac{\partial C}{\partial p} \right)_T \\ + \frac{\chi_T^2}{9} + \frac{1}{3} \left(\frac{\partial \chi_T}{\partial p} \right)_T. \end{aligned}$$

(II.4a)

$$\begin{aligned} \frac{1}{\epsilon_s} \left(\frac{\partial^2 \epsilon_s}{\partial T^2} \right)_p = \\ \frac{1}{C} \left(\frac{\partial^2 C}{\partial T^2} \right)_p - \frac{2\gamma_p}{3} \frac{1}{C} \left(\frac{\partial C}{\partial T} \right)_p \\ + \frac{\gamma_p^2}{9} - \frac{1}{3} \left(\frac{\partial \gamma_p}{\partial T} \right)_p. \end{aligned}$$

(II.4b)

Finally, we obtain the equation:

$$\begin{aligned} \frac{1}{\epsilon_s} \left(\frac{\partial^3 \epsilon_s}{\partial p^3} \right)_T = \frac{1}{C} \left(\frac{\partial^3 C}{\partial p^3} \right)_T + \frac{\chi_T}{C} \left(\frac{\partial^2 C}{\partial p^2} \right)_T + \frac{\chi_T^2}{3C} \left(\frac{\partial C}{\partial p} \right)_T + \frac{\chi_T}{3} \left(\frac{\partial \chi_T}{\partial p} \right)_T \\ + \frac{1}{C} \left(\frac{\partial \chi_T}{\partial p} \right)_T \left(\frac{\partial C}{\partial p} \right)_T + \frac{\chi_T^3}{27} + \frac{1}{3} \left(\frac{\partial^2 \chi_T}{\partial p^2} \right)_T \end{aligned} \quad (II.5)$$

APPENDIX III

Derivation of the Second Order Volumetric Derivatives of the SDC

Using equation (36) we write the operator equation:

$$\left. \frac{\partial}{\partial T} \right|_V = \left. \frac{\partial}{\partial T} \right|_P + \frac{\gamma_P}{\chi_T} \left. \frac{\partial}{\partial p} \right|_T \quad (III.1)$$

Then,

$$\begin{aligned} \left(\frac{\partial^2 \epsilon_S}{\partial T^2} \right)_V &= \left\{ \left. \frac{\partial}{\partial T} \right|_P + \frac{\gamma_P}{\chi_T} \left. \frac{\partial}{\partial p} \right|_T \right\} \left\{ \left(\left. \frac{\partial \epsilon_S}{\partial T} \right|_P + \frac{\gamma_P}{\chi_T} \left(\left. \frac{\partial \epsilon_S}{\partial p} \right|_T \right) \right) \right\} \\ &= \left(\frac{\partial^2 \epsilon_S}{\partial T^2} \right)_P + \frac{1}{\chi_T} \left(\left. \frac{\partial \gamma_P}{\partial T} \right|_P \right) \left(\left. \frac{\partial \epsilon_S}{\partial p} \right|_T \right) - \frac{\gamma_P}{\chi_T} \left(\left. \frac{\partial \epsilon_S}{\partial p} \right|_T \right) \left(\left. \frac{\partial \chi_T}{\partial T} \right|_P \right) \\ &\quad + \frac{2\gamma_P}{\chi_T} \frac{\partial^2 \epsilon_S}{\partial T \partial p} + \frac{\gamma_P^2}{\chi_T^2} \left(\left. \frac{\partial^2 \epsilon_S}{\partial p^2} \right|_T \right) + \frac{\gamma_P}{\chi_T} \left(\left. \frac{\partial \gamma_P}{\partial p} \right|_T \right) \left(\left. \frac{\partial \epsilon_S}{\partial p} \right|_T \right) \\ &\quad - \frac{\gamma_P^2}{\chi_T^3} \left(\left. \frac{\partial \chi_T}{\partial p} \right|_T \right) \left(\left. \frac{\partial \epsilon_S}{\partial p} \right|_T \right) \quad (III.2) \end{aligned}$$

The pressure derivative of the thermal expansion coefficient is not known experimentally, but may be determined via the thermodynamic

relation:

$$\left(\frac{\partial \gamma_p}{\partial p}\right)_T = - \left(\frac{\partial \chi_T}{\partial T}\right)_p \quad (III.3)$$

The final expression is then:

$$\begin{aligned} \left(\frac{\partial^2 \epsilon_s}{\partial T^2}\right)_v &= \left(\frac{\partial^2 \epsilon_s}{\partial T^2}\right)_p + \frac{1}{\chi_T} \left(\frac{\partial \gamma_p}{\partial T}\right)_p \left(\frac{\partial \epsilon_s}{\partial p}\right)_T \\ &+ \frac{2\gamma_p}{\chi_T} \frac{\partial^2 \epsilon_s}{\partial p \partial T} - \frac{2\gamma_p}{\chi_T^2} \left(\frac{\partial \epsilon_s}{\partial p}\right)_T \left(\frac{\partial \chi_T}{\partial T}\right)_p \\ &- \frac{\gamma_p^2}{\chi_T^3} \left(\frac{\partial \chi_T}{\partial p}\right)_T \left(\frac{\partial \epsilon_s}{\partial p}\right)_T + \frac{\gamma_p^2}{\chi_T^2} \left(\frac{\partial^2 \epsilon_s}{\partial p^2}\right)_T \end{aligned} \quad (III.4)$$

which is equation (40).

Equation (41) is derived using equation (37) as the operator:

$$\left(\frac{\partial}{\partial v}\right)_T = - \frac{1}{\chi_T v} \left(\frac{\partial}{\partial p}\right)_T \quad (III.5)$$

and, applying it to itself yields:

$$\begin{aligned}
 \left(\frac{\partial^2 \epsilon_s}{\partial v^2} \right)_T &= \frac{1}{\chi_T v} \left(\frac{\partial}{\partial p} \right)_T \left\{ \frac{1}{\chi_T v} \left(\frac{\partial \epsilon_s}{\partial p} \right)_T \right\} \\
 &= \frac{1}{\chi_T v} \left\{ - \frac{1}{\chi_T v} \left(\frac{\partial \epsilon_s}{\partial p} \right)_T \left(\frac{\partial \chi_T}{\partial p} \right)_T \right. \\
 &\quad \left. - \frac{1}{\chi_T v^2} \left(\frac{\partial \epsilon_s}{\partial p} \right)_T \left(\frac{\partial v}{\partial p} \right)_T + \frac{1}{\chi_T v} \left(\frac{\partial^2 \epsilon_s}{\partial p^2} \right)_T \right\} \\
 &= \frac{1}{\chi_T v^2} \left(\frac{\partial^2 \epsilon_s}{\partial p^2} \right)_T - \frac{1}{\chi_T v^2} \left(\frac{\partial \epsilon_s}{\partial p} \right)_T \left\{ \frac{1}{\chi_T} \left(\frac{\partial \chi_T}{\partial p} \right)_T - 1 \right\} \quad (\text{III.6})
 \end{aligned}$$

which is equation (41). Equation (42) is derived in a manner similar to equation (40), but this time the operator equation derived from equation (35) is:

$$\left(\frac{\partial}{\partial p} \right)_v = \left(\frac{\partial}{\partial p} \right)_T + \frac{\chi_T}{\gamma_p} \left(\frac{\partial}{\partial T} \right)_p \quad (\text{III.7})$$

and is applied to

$$\left(\frac{\partial \epsilon_s}{\partial p} \right)_v = \left(\frac{\partial \epsilon_s}{\partial p} \right)_T + \frac{\chi_T}{\gamma_p} \left(\frac{\partial \epsilon_s}{\partial T} \right)_p \quad (\text{III.8})$$

Finally, equation (43) is derived analogously to equation (41) and in this case, the operator equation is derived from equation (39) and is:

$$v \left. \frac{\partial}{\partial v} \right|_p = \frac{1}{\gamma_p} \left. \frac{\partial}{\partial T} \right|_p \quad (III.9)$$