

# TEMPERATURE DEPENDENCE OF THE DIELECTRIC CONSTANT OF IONIC CRYSTALS

by P. T. NARASIMHAN, *Department of Physics, Indian Institute of Science, Bangalore 3*

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## 1. INTRODUCTION

Although the temperature coefficients of the dielectric constant of several ionic crystals have been measured over a wide range of temperature (Eucken and Büchner, 1935), very little work has been done on the temperature dependence of the coefficients themselves. Recently, Yamashita (1951), (1952) has developed a quantum mechanical theory of the dielectric constant ( $\epsilon$ ) of an ionic crystal and has extended his theory for the calculation of the temperature coefficient  $\left(\frac{1}{\epsilon} \frac{d\epsilon}{dT}\right)$  of the dielectric constant of lithium fluoride. He has shown theoretically that the value of the coefficient for LiF is not independent of temperature. In the present investigation the variation of the quantity  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  with temperature has been experimentally determined in the case of three cubic crystals, namely, lithium fluoride, sodium chloride and magnesium oxide. The results obtained thereby have been compared with those to be expected on Yamashita's theory.

The quantum mechanical theory of Yamashita has been extended to the case of MgO for the calculation of  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  and its variation with  $T$ . For this purpose a knowledge of the values of the overlap and exchange terms occurring in the theory is essential. A simple method of evaluating these quantities has been outlined here and the details are presented below. The agreement between theory and experiment is good in the case of MgO. The reasons for the failure of the theory in the case of the highly polar crystal, LiF, have also been discussed here. Details of the theoretical calculations and experimental technique will be now presented. Atomic units have been used throughout the present calculations.

## 2. THEORETICAL

According to Yamashita (1951) the value of  $\frac{d\epsilon}{dT}$  for a crystal can be calculated from a knowledge of the change in its free energy ( $\Delta A$ ) since

$$\frac{d(\Delta A)}{dT} = -\frac{1}{2} \frac{d\chi}{dT} F^2; \quad \frac{d\epsilon}{dT} = 4\pi \frac{d\chi}{dT} \quad \dots \quad (1)$$

( $\chi$  = susceptibility). The expression for  $\frac{d(\Delta A)}{dT}$  in terms of the quantities  $a$  (inter-ionic distance),  $\rho$  (compressibility term) and  $\alpha_M$  (Madelung constant) is as follows (Yamashita, 1951).

$$\begin{aligned} \frac{d(\Delta A)}{dT} = \frac{1}{2a^3} & \left\{ 3 \left[ 2xF + \frac{1}{2} \frac{4\pi(2x)^2}{3} + \frac{4\pi(4\bar{r}^2\lambda)(2x)}{3} - \frac{2\alpha_M}{3a^2} \left( \frac{1}{\rho} - \frac{2}{a} \right) x^2 + \right. \right. \\ & + 4\bar{r}^2 F\lambda + \frac{1}{2} \frac{4\pi(4\bar{r}^2)^2\lambda^2}{3} - 3\lambda^2 - A\lambda^2 - B\lambda x \left. \right] \frac{\delta a}{a} + \\ & \left[ \frac{1}{2} \frac{4\pi(2x)^2}{3} + \frac{4\pi(4\bar{r}^2\lambda)(2x)}{3} + \frac{1}{2} \frac{4\pi(4\bar{r}^2)^2\lambda^2}{3} \right] \frac{\delta a}{a} - \\ & - \left[ \frac{2\alpha_M}{3a^2} \left( \frac{a}{\rho^2} - \frac{2}{\rho} - \frac{2}{a} \right) x^2 \right] \frac{\delta a}{a} - \left[ \frac{Aa\lambda^2}{\rho} + \frac{Ba}{\rho} \lambda x \right] \frac{\delta a}{a} + \\ & \left. + \left[ \frac{\hbar\omega}{kT^2} \cdot \frac{e^{\frac{\hbar\omega}{kT}}}{\left( e^{\frac{\hbar\omega}{kT}} - 1 \right)^2} \cdot h(\Delta\omega_x + 2\Delta\omega_y) \cdot \delta T \right] \right\} \dots \dots (2) \end{aligned}$$

The quantities  $x$  and  $\lambda$  are the perturbation parameters while the quantities  $A$  and  $B$  are the overlap and exchange terms. The last term of equation (2) is the entropy term obtained by use of the Einstein model. ( $\omega =$  Eigenfrequency).  $\bar{r}^2$  is given by the equation

$$\bar{r}^2 = \int_0^a |P(r)|^2 r^2 dr \dots \dots \dots (3)$$

where  $P(r)$  is the probability term in the wave function. If  $\psi_0$  is the unperturbed wave function and  $\psi$  the perturbed wave function we have according to Kirkwood (1932)

$$\psi = \psi_0(1 + \lambda r \cos \theta) \dots \dots \dots (4)$$

( $\lambda =$  perturbation parameter). For actual calculation of  $\frac{d\epsilon}{dT}$  we need the values of  $\bar{r}^2$ ,  $x$  and  $\lambda$  as well as those of  $A$  and  $B$ . The compressibility data on the crystal under consideration are also required for the evaluation of  $\rho$  (Yamashita, 1952). Yamashita has calculated the values of  $\bar{r}^2$ ,  $A$  and  $B$  by directly evaluating the corresponding integrals. The values thus arrived at are, in general, not self-consistent since the calculated and observed values of the dielectric constant do not agree. One of the main reasons for this discrepancy lies with the difficulty in the choice of an accurate wave function for an ion in a crystal. Owing to this fact in the present paper we have used the observed value of the dielectric constant in order to arrive at the values of the parameters.

### 3. VALUES OF THE PARAMETERS AND THE CALCULATION OF $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$

For the evaluation of  $\bar{r}^2$  we proceed as follows. The polarisability  $\alpha_f$  of an ion in the free state is related to  $\bar{r}^2$  by the equation

$$\alpha_f = \frac{(4\bar{r}^2)^2}{6} \dots \dots \dots (5)$$

The values of  $\alpha_f$  have been already given by Pauling (1927) who has calculated these values on a quantum mechanical basis. Using the value of  $\bar{r}^2$  thus obtained

we next proceed to calculate the value of the overlap term  $A$ . Now, the change in the total energy ( $\Delta E_0$ ) of an ionic crystal in a high frequency field is given by the equation (Yamashita, 1952)

$$\Delta E_0 = -4\bar{r}^2 F\lambda - \frac{1}{2} \frac{4\pi}{3} \frac{(4\bar{r}^2)^2}{2a^3} \lambda^2 + 3\lambda^2 + A\lambda^2 \quad \dots \quad (6)$$

We have also

$$\Delta E_0 = -\frac{1}{2} \chi_0 F^2; \epsilon_0 = 1 + \frac{4\pi\chi_0}{2a^3} \quad \dots \quad (7)$$

( $\epsilon_0$  = dielectric constant in the high frequency field). Equation (6) may be written in the form

$$\Delta E_0 = -4\bar{r}^2 F\lambda + N\lambda^2 \quad \dots \quad (8)$$

By the variational principle we have  $\frac{\partial \Delta E_0}{\partial \lambda} = 0$

Therefore,

$$N\lambda = 2\bar{r}^2 F \quad \dots \quad (9)$$

Inserting this value of  $N\lambda$  in equation (8) we can calculate the value of  $N$  since the value of  $\Delta E_0$  can be obtained from equation (7) using the observed value of  $\epsilon_0$ . Needless to say, the value of  $A$  is easily obtained once the value of  $N$  is known.

From the known values of  $\bar{r}^2$  and  $A$  we can evaluate the exchange term  $B$  as follows. We make use of the expression given by Yamashita (1952) for the change ( $\Delta E$ ) in the total energy of a crystal in a static field. As stated earlier the value of  $\rho$  occurring in the equation can be obtained from the compressibility data. Substituting the values of  $\bar{r}^2$ ,  $A$  and  $\rho$  in Yamashita's equation we calculate the value of  $\Delta E$  by giving  $B$  different values (ranging usually from  $-1$  to  $+1$ ). The values of  $\Delta E$  thus calculated are plotted against the respective  $B$  values when a smooth curve is obtained. From the observed static dielectric constant of the crystal the true value of  $\Delta E$  can be obtained from an equation similar to (7). Thus the value of  $B$  corresponding to the true value of  $\Delta E$  can be found from the graph. Although the above methods of calculating the values of  $\bar{r}^2$ ,  $A$  and  $B$  are phenomenological they are quite accurate on account of their self-consistency and are also simple since the values of these parameters are obtained without tedious evaluation of the integrals.

The value of  $A$  for LiF obtained by the present method is 1.76 ( $\bar{r}^2 = 1.90$ ). This value of  $A$  is nearly twice that ( $A = 0.8$ ) given by Yamashita. The present value of  $A$  is more consistent with experimental data and since this parameter may be viewed upon as a correction term this new value of  $A$  is to be preferred. Similarly in the case of MgO the value of  $A$  obtained here is 3.51 as compared to Yamashita's value of 1.9 only. It may be pointed out here that the value of the dielectric constant for high frequency field calculated by the use of Yamashita's values is very much higher than the observed values. [LiF:  $\epsilon_0 = 2.33$  (calculated) 1.92 (observed); MgO:  $\epsilon_0 = 4.56$  (calcd.) 2.95 (observed).] However, good agreement is obtained with regard to the value of  $\bar{r}^2$ . The value of  $\bar{r}^2$  for MgO obtained by the present method is 3.14 as compared to Yamashita's value of 3.19. In the case of LiF, the value of  $B = 0.52$  obtained by the present method agrees very well with that ( $B = 0.50$ ) obtained by Yamashita by direct evaluation of the integrals. As pointed out earlier, since the values of  $A$  and  $B$  obtained by the use of the experimental data on dielectric constants are self-consistent, these values are to be preferred in the calculations of the temperature coefficients of dielectric constant.

Table I and Fig. 1 show the method of calculation of  $B$  for LiF. The observed value for the static dielectric constant being 9.27 (Mott and Gurney, 1940) the value of  $\Delta E$  corresponding to this is  $-35.5 F^2$ . From Fig. 1 it will be seen that the value

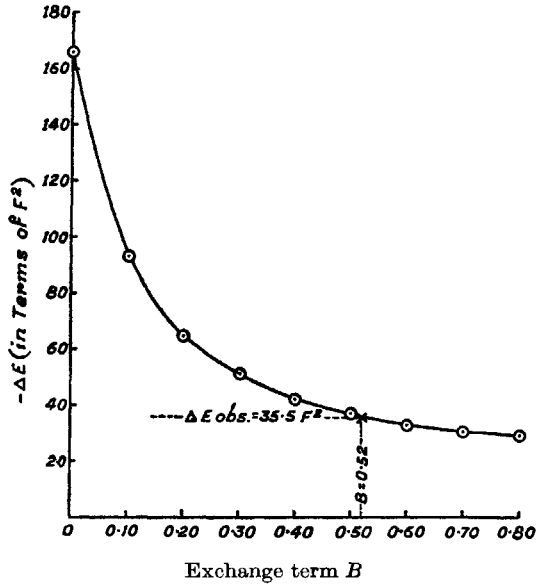


FIG. 1. Variation of  $\Delta E$  with  $B$   
Lithium fluoride

of  $B$  for this value of  $\Delta E$  is 0.52. Table II and Fig. 2 show similarly the  $\Delta E$  and  $B$  values for MgO. The observed static dielectric constant of MgO being 9.8 the

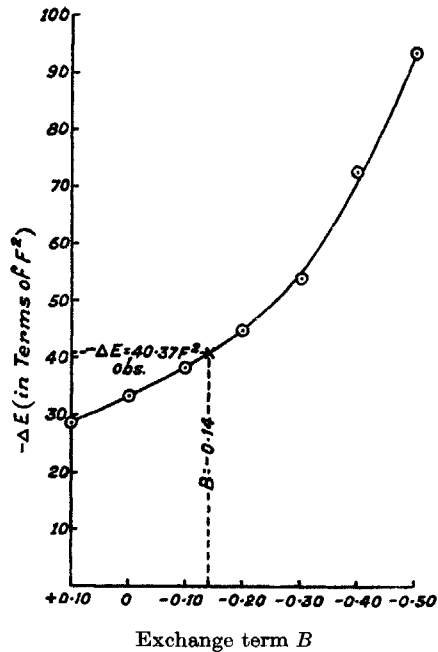


FIG. 2. Variation of  $\Delta E$  with  $B$   
Magnesium oxide

value of  $\Delta E = -40.37 F^2$ . From Fig. 2 we find that the value of  $B$  corresponding to this  $\Delta E$  value is  $-0.14$ . The values of  $\lambda$  and  $x$  given in Tables I and II are obtained by the use of the variational condition  $\frac{\partial \Delta E}{\partial \lambda} = 0$ ;  $\frac{\partial \Delta E}{\partial x} = 0$ .

TABLE I  
*B and  $\Delta E$  values for LiF.*

$B$	$\lambda$	$x$	$\Delta E$
0	11.00 $F$	124.40 $F$	-166.15 $F^2$
0.10	5.71 $F$	70.31 $F$	-92.00 $F^2$
0.20	3.70 $F$	50.47 $F$	-64.56 $F^2$
0.30	2.62 $F$	40.45 $F$	-50.45 $F^2$
0.40	1.92 $F$	34.69 $F$	-42.00 $F^2$
0.50	1.41 $F$	31.22 $F$	-36.57 $F^2$
0.60	0.985 $F$	29.22 $F$	-32.97 $F^2$
0.70	0.599 $F$	28.42 $F$	-30.70 $F^2$
0.80	0.200 $F$	28.89 $F$	-29.48 $F^2$

TABLE II  
*B and  $\Delta E$  values for MgO*

$B$	$\lambda$	$x$	$E$
0.10	2.72 $F$	12.24 $F$	-29.33 $F^2$
0	3.05 $F$	13.92 $F$	-33.10 $F^2$
-0.10	3.49 $F$	16.09 $F$	-37.97 $F^2$
-0.20	4.07 $F$	19.01 $F$	-44.55 $F^2$
-0.30	4.90 $F$	23.15 $F$	-53.93 $F^2$
-0.40	6.18 $F$	29.49 $F$	-72.15 $F^2$
-0.50	8.40 $F$	40.46 $F$	-93.20 $F^2$

Table III gives the values of  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  for LiF calculated by the use of equations (1) and (2) with and without the entropy term. In Table IV the values of  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  of

TABLE III  
 $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  of LiF (*Theoretical*)

Temp. Range °C.	$\frac{1}{\epsilon} \frac{d\epsilon}{dT}$ calcd. ( $\Delta S$ term neglected)	$\frac{1}{\epsilon} \frac{d\epsilon}{dT}$ calcd. ( $\Delta S$ term included)
27-127 ..	$49.0 \times 10^{-5}$	$35.0 \times 10^{-5}$
127-227 ..	$56.5 \times 10^{-5}$	$40.5 \times 10^{-5}$
227-327 ..	$64.0 \times 10^{-5}$	$46.0 \times 10^{-5}$
327-527 ..	$75.5 \times 10^{-5}$	$56.0 \times 10^{-5}$
527-727 ..	$91.0 \times 10^{-5}$	$70.5 \times 10^{-5}$

MgO are given and these have been calculated without the entropy term which is rather uncertain. The thermal expansion data of Eucken and Dannöhl (1934) on LiF and of Austin (1931) on MgO have been used in the calculations.

TABLE IV

$$\frac{1}{\epsilon} \frac{d\epsilon}{dT} \text{ of MgO (Theoretical)}$$

Temp. Range °C.	$\frac{1}{\epsilon} \frac{d\epsilon}{dT}$ calcd. ( $\Delta S$ term neglected)
25-50 ..	$13.5 \times 10^{-5}$
50-100 ..	$16.0 \times 10^{-5}$
100-150 ..	$19.6 \times 10^{-5}$
150-200 ..	$21.5 \times 10^{-5}$
200-250 ..	$22.5 \times 10^{-5}$

It will be seen from Tables III and IV that in the case of LiF and MgO a variation in the value of  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  with  $T$  is to be expected. We shall now give the details of the experimental method for the determination of the temperature coefficient of the dielectric constant of crystals at various temperatures and then we shall see how far the predictions of the theory are in accord with experimental results.

#### 4. EXPERIMENTAL

The capacity measurements were made with a heterodyne beat apparatus which has been already described elsewhere (Narasimhan, 1953). The A.C. power supply for the apparatus was obtained through a constant voltage transformer. The beat note was extremely steady after a warm-up period of 3 to 4 hours. The changes in the capacity brought about by changes in temperature were measured by means of a stepped-rod type condenser (Watson, Rao and Ramaswamy, 1939). This condenser was placed in parallel with the crystal condenser which consisted of a brass container (3" diameter;  $2\frac{1}{2}$ " height;  $\frac{5}{8}$ " thick) with a removable lid screwed on top. This assembly was first silvered and then given a thick coating of gold in the interior. In the inside bottom of the cell was mounted a circular piece of ceramic insulator on which was screwed a gold plated brass disc ( $1\frac{1}{2}$ " diameter;  $\frac{1}{8}$ " thick) carrying a terminal for connecting the r.f. lead. The crystal under investigation was placed on the disc after aluminising the broad parallel surfaces of the crystal plate. The contact for the earth electrode of the crystal plate was obtained by a metal probe connected to the brass cell. The lead from the terminal of the brass disc was taken out through a hole ( $\frac{1}{2}$ " diameter) made at the side of the outer brass vessel. Covering this hole was a ceramic insulator carrying a terminal to which was connected the above-mentioned lead from the insulated disc. The crystal cell could be heated by means of a wire resistance heater strip placed at the outside bottom of the cell. The cell was connected to the heterodyne beat apparatus by means of a shielded cable with the outer brass vessel forming the earthed electrode.

Temperatures were measured by means of a thermocouple. Since the difference in temperature between the inner brass disc and the outer brass vessel

was found to be less than  $0.5^{\circ}\text{C}$ . over the range employed it was found convenient to place the thermocouple on the outer wall of the cell for purposes of temperature measurement. Regulation at desired temperatures was carried out by means of an electronic relay in conjunction with a 'contact head' which was operated by means of the expansion of the brass cell itself. The regulation thus obtained was within  $1^{\circ}\text{C}$ . In the present investigation we have worked up to  $250^{\circ}\text{C}$ . only partly on account of the fact that the capacity changes up to this range only could be followed by the Watson condenser in one continuous experiment and partly on account of the fact that the aluminised surfaces of the crystal tended to 'crack-up' into flakes at higher temperatures. The experimental procedure comprised of firstly the determination of the capacity change of the empty cell over the desired temperature range and then the determination of the capacity change over the same temperature range with the crystal plate inside the cell. The difference in the readings gives the capacity change ( $\Delta C$ ) due to the crystal plate in arbitrary condenser units and thus the value of  $\frac{\Delta C}{\Delta T}$  could be obtained. The  $\Delta C$  values were checked up by taking the readings both on heating and cooling when reproducible results could be obtained. In the present work the value of the capacity ( $C$ ) of the crystal plate in arbitrary condenser units was obtained at room temperature by direct measurement and subsequent capacity ( $C$ ) values at different temperatures have been obtained by the addition of the corresponding  $\Delta C$  values. According to Eucken and Büchner (1935)  $\frac{1}{\epsilon} \frac{d\epsilon}{dT} = \frac{1}{C} \frac{\Delta C}{\Delta T} - \alpha$  where  $\alpha$  is the coefficient of linear expansion of the crystal.

Thus using the known values of  $\alpha$  we have obtained the value of  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  from the capacity data. The error in the values of  $\frac{1}{C} \frac{\Delta C}{\Delta T}$  reported here is estimated to be  $\pm 0.2 \times 10^{-5}$  corresponding to an error of 2-3 divisions in the measuring condenser settings.

LiF and MgO crystals used in the present work were clear crystals grown from the melt while the NaCl crystal used was a flawless natural one.

## 5. RESULTS

The experimental results on the dependence of  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  on  $T$  for LiF, NaCl and MgO are given in Tables V, VI and VII. The capacity readings are in arbitrary condenser units.

TABLE V

$\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  of LiF in the temperature range  $25^{\circ}\text{C}.$ - $250^{\circ}\text{C}.$

Temp. Range $^{\circ}\text{C}.$	Cap. change due to cell $\Delta C$ (cell)	Cap. change with LiF <sup>a</sup>	$\Delta C$	Initial cap. $C$	$\frac{1}{C} \frac{\Delta C}{\Delta T}$ $\times 10^5$	$\alpha \times 10^5$	$\frac{1}{\epsilon} \frac{d\epsilon}{dT}$ $\times 10^5$
25- 50 ..	364	1,338	974	105,726	35.4	3.6	31.8
50-100 ..	971	3,398	2,427	106,700	45.5	3.9	41.6
100-150 ..	1,122	3,925	2,803	109,127	51.3	4.2	47.1
150-200 ..	2,657	6,072	3,415	111,930	61.0	4.5	56.5
200-250 ..	5,836	9,909	4,073	115,345	70.6	4.8	65.8

TABLE VI

 $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  of NaCl in the temperature range 25°C.-250°C.

Temp. Range °C.	Cap. change due to cell $\Delta C$ (cell)	Cap. change with NaCl	$\Delta C$	Initial cap. $C$	$\frac{1}{C} \frac{\Delta C}{\Delta T} \times 10^5$	$\alpha \times 10^6$	$\frac{1}{\epsilon} \frac{d\epsilon}{dT} \times 10^5$
25- 50 ..	406	740	334	33,768	39.6	4.04	35.6
50-100 ..	902	1,674	772	34,102	45.3	4.05	41.3
100-150 ..	2,235	3,213	978	34,874	56.1	4.06	52.0
150-200 ..	5,088	6,285	1,197	35,852	66.8	4.08	62.7
200-250 ..	8,456	9,806	1,350	37,049	72.9	4.09	68.8

TABLE VII

 $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  of MgO in the temperature range 25°C.-250°C.

Temp. Range °C.	Cap. change due to cell $\Delta C$ (cell)	Cap. change with MgO	$\Delta C$	Initial cap. $C$	$\frac{1}{C} \frac{\Delta C}{\Delta T} \times 10^5$	$\alpha \times 10^6$	$\frac{1}{\epsilon} \frac{d\epsilon}{dT} \times 10^5$
25- 50 ..	406	581	175	46,364	15.1	0.67	14.4
50-100 ..	902	1,290	388	46,539	16.7	0.79	15.9
100-150 ..	2,235	2,690	455	46,927	19.4	0.97	18.4
150-200 ..	5,088	5,637	549	47,382	23.2	1.06	22.1
200-250 ..	8,456	9,036	574	47,931	24.0	1.11	22.9

The  $\Delta C$  (cell) values for NaCl and MgO are different from those for LiF owing to a few alterations made in the original cell for purposes of accommodating the larger NaCl and MgO crystals.

## 6. DISCUSSION

The variations of  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  with  $T$  for LiF, NaCl and MgO have been shown graphically in Figs. 3-5. It will be seen that the experimentally observed variation of

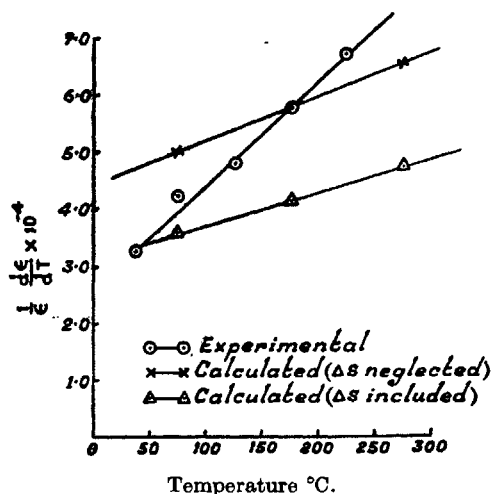


FIG. 3. Variation of  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  of LiF with temperature



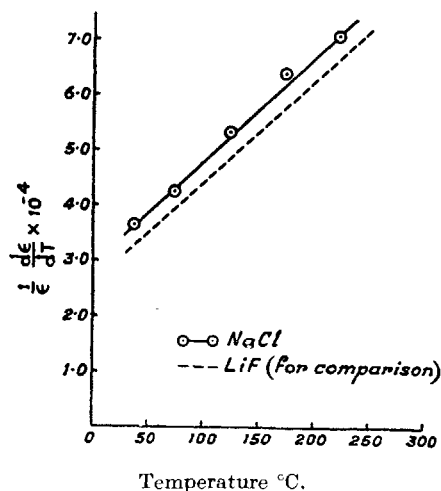


FIG. 4. Variation of  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  of NaCl with temperature

$\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  of LiF is much larger than that theoretically predicted (both with and without  $\Delta S$  term). The temperature dependence of the coefficient in the case of NaCl follows very closely that observed for LiF (see Fig. 4). The coefficient in the

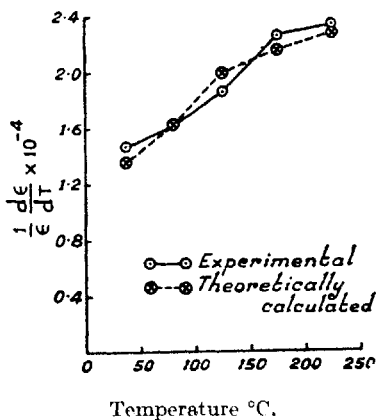


FIG. 5. Variation of  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  of MgO with temperature

case of NaCl is displaced towards larger values. This shift may be qualitatively accounted for on the basis of the polar nature of the crystals as has been shown by Eucken and Büchner. In the case of MgO, however, the agreement between theory and experiment is quite satisfactory considering the neglect of the  $\Delta S$  term.

Of the reasons for the discrepancy between theory and experiment in the case of the ionic crystals like LiF we may mention here the neglect of long range forces in the theory. In other words, only the nearest neighbours of an ion are considered. Further, the calculation of the repulsive energy term from compressibility data

may not be accurate. It must be also stated that the use of the Einstein model for the calculation of the  $\Delta S$  term makes the calculations approximate. Above all the variations in the  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  values are theoretically obtained because of variations in the thermal expansion coefficient. In this respect the variations in the thermal expansion coefficient seem to govern ultimately the  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  values since it will be seen from equation (2) that the value of  $\frac{\delta a}{a}$  is used for multiplication. The experimental results do not seem to favour this relationship at least in the case of LiF. It is interesting to note here that while the  $\alpha$  values of NaCl do not vary much the  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  values are profoundly influenced by temperature change (refer Table VI).

From the observed variation of  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  with  $T$  in the three crystals under consideration the following empirical expression may be deduced

$$\frac{1}{\epsilon} \frac{d\epsilon}{dT} \cdot \frac{1}{T^{3/2}} = \text{constant. } T = ^\circ\text{K.} \quad \dots \quad (10)$$

As will be seen from Table VIII equation (10) represents the variation of the  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  values to a fair degree of accuracy. The value of the constant is of course characteristic of the crystal.

TABLE VIII

For LiF, NaCl and MgO

Temp. Range °C.	$\frac{1}{\epsilon} \frac{d\epsilon}{dT} \cdot \frac{1}{T^{3/2}}$		
	LiF	NaCl	MgO
25-50 ..	0.058	0.065	0.026
50-100 ..	0.064	0.064	0.025
100-150 ..	0.059	0.066	0.023
150-200 ..	0.060	0.066	0.023
200-250 ..	0.059	0.062	0.021

It must be emphasized here that the basis of equation (10) is purely empirical. But considering the constancy of the values obtained in Table VIII the equation seems to represent a true relationship at least for LiF and NaCl. The values obtained for MgO are progressively lower with increasing temperature but further work at higher temperatures is needed in order to throw more light on this aspect of the problem.

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## ABSTRACT

The temperature coefficient  $\left(\frac{1}{\epsilon} \frac{d\epsilon}{dT}\right)$  of the dielectric constant of LiF, NaCl and MgO has been measured over the temperature range 25°C.-250°C. It is shown that the value of the coefficient itself is dependent on temperature. The quantum mechanical theory of Yamashita has been used for the theoretical calculation of the values of  $\frac{1}{\epsilon} \frac{d\epsilon}{dT}$  at different temperatures. From the present experimental data the above theory is shown to fail in the case of LiF while in the case of MgO good agreement is obtained. The drawbacks of the theory have also been discussed in the light of the above data. An empirical relationship between the value of the temperature coefficient of ionic crystals and the temperature has been pointed out.

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